ABSTRACT

KLOXIN, CHRISTOPHER JAMES. Investigating Aqueous PEO-PPO-PEO Triblock Copolymer Dispersion Dynamics with Colloidal Sphere Thermal Motion. (Under the direction of John H. van Zanten.)

The objective of the dissertation is to investigate the structural and dynamical behavior of aqueous poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock surfactant dispersions, commercially known as PluronicsTM, by studying the Brownian or thermal motion of embedded tracer probe particles. Recent advances in the understanding of diffusive light transport in highly scattering media seeded a novel dynamic light scattering technique in the multiple scattering limit known as diffusing wave spectroscopy (DWS). This technique allows for the determination of probe motion at frequencies greater than 1 MHz and at a spatial resolution of several angstroms. Thus, DWS provides unique access to early thermal relaxation modes in complex fluids that are the proposed origin of viscoelastic behavior observed on a macroscopic level.

In general, Pluronic-type macromolecular surfactants associate into spherical micelles when dispersed in aqueous solution, leading to complex structures and rich dynamic behavior. In the first part of the dissertation, we demonstrate the utility of DWS microrheology by investigating the short-time dynamics of aqueous Pluronic L64 [(EO)13(PO)30(EO)13] solutions, revealing a temperature independent high frequency viscosity above the micellization temperature. The dynamics at high temperatures are dominated by an apparent attractive inter-micellar potential, consistent with our inverse osmotic pressure measurements. We directly confirm the presence of a short-lived elastic gel at high temperatures, which previously could only be inferred by extrapolating traditional mechanical rheometry measurements. We attribute the existence of this short-lived elastic gel to sample spanning clusters indicating the crossing of a dynamic percolation threshold.

In the second part of this dissertation, we utilize a high-pressure scattering cell to examine the pressure-temperature phase space of aqueous Pluronic P85 [(EO)25(PO)40(EO)25] solutions. We demonstrate that subtle changes in water by densification via increased hydrostatic pressure, by increasing thermal energy, or even by isotopic substitution, lead to discernable large-scale effects in aqueous P85 Pluronic samples. More generally, we demonstrate the utility of DWS colloidal sphere thermal motion studies to explore complex fluids in high pressure and temperature environments, allowing for the construction of phase diagrams based on dynamical pathways.
INVESTIGATING AQUEOUS PEO-PPO-PEO TRIBLOCK COPOLYMER DISPERSION DYNAMICS WITH COLLOIDAL SPHERE THERMAL MOTION

by

CHRISTOPHER JAMES KLOXIN

A dissertation submitted to the Graduate Faculty of
North Carolina State University
In partial fulfillment of the
Requirements for the degree of
Doctor of Philosophy

in

CHEMICAL ENGINEERING

Raleigh, NC
2006

Approved by:

Prof. John H. van Zanten
(Chair of Advisory Committee)

Prof. Christopher R. Daubert
Prof. Carol K. Hall

Prof. Saad A. Khan
Prof. Michael Rubinstein
Biography

Christopher J. Kloxin was born September 22, 1976, in Greeley, Colorado. He is the son of Cole and Mary Busha and James and Kellie Kloxin and has three brothers, Nick Kloxin, West Busha, and Ross Busha. He received a B.S. in Chemical Engineering from the University of Colorado, Boulder, in May 1999. From May 1999 to August 2000 he worked at Eastman Kodak Company in the polymer science and technology research labs in Rochester, NY. In August 2000, he was admitted to North Carolina State University to pursue his doctoral studies in Chemical Engineering.
Acknowledgements

First, I thank my thesis advisor John van Zanten for his support, guidance, and friendship. He has given me the freedom to develop into the independent researcher I am today. Also, he went beyond the typical advisor role by helping me start and stop experiments, allowing data to be taken almost 24 hours a day over several months. Additionally, he waded through several early drafts of this dissertation, helping fine tune the text into its current state. I consider John to be a good friend and will look back fondly on my experience in his group.

There are several people who have played an important role in supporting and encouraging me as a graduate student. Some of them will inevitably, and not deliberately, go unnamed. I would like to recognize the help and efforts of the past and current undergraduate and graduate students in the van Zanten group: Samiul Amin, Jamie Arroway, Shaun Tanner, Chris Smith, and David Brandner. I thank the Khan group for graciously granting me time on their rheometers; in particular, I thank Angelica Sanchez for training and for the many “microrheology versus bulk rheology” discussions. Additionally, Angelica Sanchez and April Kloxin were subject to the roughest drafts of this thesis, making several suggestions that significantly contributed to its readability and flow. Last, I have to thank Brian Price for being a constant check to the validity of my work and thought process. To a large extent, my pursuit in research of complex phenomenon is due to his contagious enthusiasm for the science and his further belief in my abilities.

I am tremendously grateful for the support of my friends and family. Their constant friendship and love have injected calm and sanity to this life of stochastic research. I am fortunate to have two great sets of parents, Cole and Mary Busha and James and Kellie Kloxin. They have always held whatever it is that I do in high regard and provided an oxymoronic balance of indifference and encouragement, giving me the confidence that no matter what I did it would be great. Finally, there is no way that I can express the appreciation I have for my wife, April, who has been my anchor throughout my graduate career. Her love has shown me that there is life beyond the world of science and that it is truly beautiful.
Table of Contents

List of Tables  vii

List of Figures  viii

List of Symbols and Notations  xii

Chapter 1  Introduction to DWS and Method  1

1.1  PCS to DWS ............................................................................................................................. 1
1.1.1  Single Scattering ................................................................................................................ 2
1.1.2  The Autocorrelation Function and Speckle ................................................................. 5
1.1.3  From Single to Multiple Scattering................................................................................ 8
1.1.4  Comparison ......................................................................................................................12
1.2  DWS Analysis ......................................................................................................................... 13
1.2.1  Experimental Setup.......................................................................................................... 14
1.2.1.1  Pressure/Temperature Scattering Cell...................................................................... 16
1.2.2  Experimental Considerations ........................................................................................... 17
1.2.2.1  The Dynamical Contrast: Fitting the Siegert Relationship..................................... 18
1.2.2.2  Diffuse Reflectivity at the Boundary ........................................................................ 19
1.2.2.3  Errors in the Transport Mean Free Path, \( l^* \) .......................................................... 20
1.2.2.4  The Diffusing Approximation: \( L/l^* \) ................................................................. 23
1.2.2.5  Pressure and Temperature Corrections....................................................................... 25
1.2.3  Summary .......................................................................................................................... 26

Appendix 1.A  Maxwell’s Equations .......................................................................................... 27
Appendix 1.B  Intensity Autocorrelation Function and the Siegert Relationship ................ 28
Appendix 1.C  Multiple Scattering Phase Difference............................................................... 30
Appendix 1.D  The Diffusion Equation....................................................................................... 32
Appendix 1.D.a  Initial Conditions ............................................................................................. 33
Appendix 1.D.b  Boundary Conditions....................................................................................... 33
Appendix 1.D.c  The Solution to the Diffusion Equation in Cylindrical Coordinates............. 36
Appendix 1.D.d The Solution to the Telegrapher Model in Cylindrical Coordinates ............................................................................................... 41
Appendix 1.E Calculating Reflectivity........................................................................................................................................................................ 42
Appendix 1.E.a Consideration of Total Internal Reflectance .......................................................................................................................... 43
Appendix 1.F Numerical Calculation of l* ............................................................................................................................................................ 43
Appendix 1.G Numerical Conversion of \( g_1(\tau) \) to \( \Delta r^2(\tau) \) .................................................................................................................. 44
References ................................................................................................................................................................................................................. 46

Chapter 2 Probe Particle Dynamics 48

2.1 A Brief Historical Account of Brownian Motion ........................................................................................................................................ 48
2.2 Einstein’s Description of Brownian Motion .............................................................................................................................................. 49
2.3 A Microscopic Description of Single Sphere Thermal Fluctuations .................................................................................................. 50
2.3.1 The Solution to the Langevin Equation ........................................................................................................................................... 51
2.3.2 A Probabilistic Approach: The Smoluchowski Equation ................................................................................................................... 53
2.4 Inertia and Hydrodynamic Effects ............................................................................................................................................................. 54
2.4.1 Comparison of the Extended and Simplified Langevin Equations .................................................................................................. 57
2.5 DWS Measurement of Spheres in Water Over a Range of Temperature and Pressure ....................................................................................................................................................................................... 59
2.6 Fluctuation-Dissipation Formalism ............................................................................................................................................................. 63
Appendix 2.A Einstein’s Classic Derivation ..................................................................................................................................................... 66
Appendix 2.B The Mean Squared Displacement and the Velocity Autocorrelation Function ......................................................................................................................................................................................... 67
Appendix 2.C The Mean Momentum and Position Coordinate from the Langevin Equation .................................................................................................................................................................................................... 70
Appendix 2.D The Extended Langevin Equation .............................................................................................................................................. 74
Appendix 2.D.a Limiting Behavior ................................................................................................................................................................. 74
Appendix 2.D.b Solution to the Extended Langevin Equation .......................................................................................................................... 76
Appendix 2.D.c The Calculation of the Complex Complementary Error Function ................................................................................................................................. 78
Appendix 2.E The Generalized Langevin Equation and Linear Viscoelastic Functions .................................................................................................................................................................................................... 79
Appendix 2.E.a Linear Viscoelastic Functions .................................................................................................................................................... 80
Appendix 2.E.b Transformation of Linear Viscoelastic Functions .................................................................................................................. 82
References ................................................................................................................................................................................................................. 84
Chapter 3  Pluronic L64

3.1 Introduction ........................................................................................................................... 87

3.2 Experimental Methods and Results ....................................................................................... 88
   3.2.1 Sample Information and Preparation ............................................................................. 88
   3.2.2 90° Static Light Scattering ........................................................................................... 88
   3.2.3 Bulk Viscosity Measurements ....................................................................................... 92
   3.2.4 Probe Particle Dynamics in L64 ..................................................................................... 94

3.3 Discussion .............................................................................................................................100
   3.3.1 Viscoelasticity in Dispersion of Hard Spheres ...............................................................100
   3.3.2 Adhesive Hard Sphere Model and Percolation ..............................................................103
   3.3.3 Beyond the Adhesive Hard Sphere Model .....................................................................107

3.4 Conclusion .............................................................................................................................108

References ......................................................................................................................................110

Chapter 4  Pluronic P85

4.1 Introduction ..........................................................................................................................114

4.2 Experimental Methods..........................................................................................................116
   4.2.1 Sample Information and Preparation ............................................................................117

4.3 Unimer-to-micelle Transistion, 5 wt% P85 ........................................................................118

4.4 The Micellar Crystalline Phase, 25 wt% P85 ......................................................................121
   4.4.1 The Solubility of Ethylene oxide-Based Polymers.........................................................123
   4.4.2 The isotopic effect: D₂O versus H₂O ...........................................................................123
   4.4.3 Dynamical Behavior of 25 wt% P85 in D₂O at Ambient Pressure .................................126
   4.4.4 Hydrostatic Pressure Influence on the Dynamical Behavior of 25 wt% P85 in D₂O .........127
   4.4.5 The Dynamical Phase Diagram of 25 wt% P85 in D₂O .................................................130

4.5 The Micellar Crystalline Phase – Take II, 35 wt% P85 .......................................................131
   4.5.1 Transitions into the Micellar Crystal 35 wt% P85 in H₂O ..........................................133
   4.5.2 Light Transmission and 90° Static Light Scattering Measurements at Ambient Pressure .............................................. 135
   4.5.3 High Pressure Dynamical Phase Diagram of 35 wt% P85 in H₂O ......................... 138
   4.5.4 High Temperature Isotherm ........................................................................................ 139

4.6 Summary and Conclusion .....................................................................................................141

References ......................................................................................................................................143
List of Tables

Chapter 1 Introduction to DWS and Methods

1.1 The physical parameters for a 1 wt% 420 nm polystyrene spheres in water estimated using a multi-parameter model for water and the approximations for polystyrene as mentioned in the text .................. 26
List of Figures

Chapter 1  Introduction to DWS and Methods

1.1 Illustration of single scattering setup. ................................................................. 3

1.2 Speckle pattern created from the constructive and destructive
    interference of scattered light.................................................................................. 5

1.3 Hypothetical Intensity trace at a fixed detector position................................. 6

1.4 Description of an arbitrary photon path in random media............................ 9

1.5 Typical transmission mode DWS setup........................................................... 15

1.6 The experimental setup...................................................................................... 16

1.7 High-pressure scattering cell.......................................................................... 17

1.8 The effect of the dynamical contrast on the conversion from \( g_1(\tau) \)
    to \( \langle \Delta r^2(\tau) \rangle \)....................................................................................... 19

1.9 The effect of the boundary reflectivity on the conversion from \( g_1(\tau) \)
    to \( \langle \Delta r^2(\tau) \rangle \)....................................................................................... 20

1.10 The transmission of diffusing light as a function of \( L/l^* \) with and
    without reflectivity............................................................................................... 21

1.11 The effect of \( l^* \) on the conversion from \( g_1(\tau) \) to \( \langle \Delta r^2(\tau) \rangle \)...................... 22

1.12 The effect of \( L/l^* \) on the conversion from \( g_1(\tau) \) to \( \langle \Delta r^2(\tau) \rangle \)...................... 23

1.13 Comparison of the telegrapher and diffusion equations for \( L/l^* \) less
    than 12................................................................................................................. 24

1.14 Scattering geometry used to calculated the photon flux........................... 33
Chapter 2  Probe Particle Dynamics

2.1  Comparison of the simplified Langevin equation and the extended Langevin equation for the mean square displacement, the velocity autocorrelation function normalized by the initial velocity, and the time-dependent diffusion coefficient normalized by the long-time diffusion coefficient for 1 µm diameter polystyrene spheres in water at 20°C ............................................................... 58

2.2  Comparison with theoretically predicted mean square displacement by the simplified and the extended Langevin equations versus experimental DWS data for 1 wt% 420 nm polystyrene spheres in water at 21°C ........................................................................................................ 60

2.3  The mean square displacement for 32 data sets taken over a temperature range of 20 to 80°C and a pressure range of 0 to 241 MPa for a sample of 1 wt% 421 nm diameter polystyrene spheres in water ................................................................................ 61

2.4  Extended Langevin equation fit to the mean square displacement for 420 nm spheres in water from 20 to 80°C. Inset shows the viscosity autocorrelation function scaling algebraically .............................................. 62

Chapter 3  Pluronic L64

3.1  Estimated inverse osmotic compressibility for L64 as a function of temperature .............................................................................................................................................. 90

3.2  Image demonstrating the presence of large aggregates found in a sample of 20 wt% L64 in water at 20°C ........................................................................................................ 91

3.3  Images showing the cloud point envelope at higher temperatures................................................. 92

3.4  Bulk viscosity measurements for concentration of 5 to 40 wt% L64 in water over a temperature ramp from 20 to 60°C ................................................................. 93

3.5  Comparison of the bulk viscosity measurement to the zero frequency viscosity obtained from DWS comparison over concentration and temperature ........................................................................................................ 95
3.6 Mean square displacement traces for L64 concentrations at 20°C and 50°C

3.7 Comparison of the microscopic creep for six concentrations from 5 to 30 wt% L64 in water over a range of temperatures

3.8 Bulk viscosity measurements compared to the high frequency viscosity

3.9 The normalized loss and storage components of the complex viscosity for a sample of 25 wt% L64 in water at 45°C, 50°C, 54°C, and 57°C

3.10 $1/\tau-\phi$ phase diagram predicted using the Baxter adhesive hard sphere model exhibiting LCST behavior

3.11 Elastic and viscous moduli for 20 wt% L64 compared over a range of temperatures

3.12 Elastic and viscous moduli for a range of concentrations at the highest temperature considered (57°C)

Chapter 4  Pluronic P85

4.1 Sketch of a Pluronic micelle highlighting an individual PEO-PPO-PEO chain spanning the micellar core

4.2 Microscopic creep data for 5 wt% P85 in water at ambient pressure over a range of temperatures

4.3 Microscopic creep data for 5 wt% P85 sweeping in pressure at the 20°C, 40°C, and 70°C isotherms

4.4 Effect of pressure and temperature on the dynamical behavior of 5 wt% P85 in H$_2$O

4.5 Microscopic creep data for 25 wt% P85 in H$_2$O from 20 to 35°C and 40 to 60°C

4.6 Zero frequency viscosity for 25 wt% P85 samples for different solvent ratios of H$_2$O to D$_2$O
4.7 Microscopic creep data for 25 wt% P85 in D₂O at ambient pressure as a function of temperature ................................................................. 126

4.8 Microscopic creep data for 25 wt% P85 in D₂O along the 20°C, 35°C, 45°C, and 70°C isotherms ........................................................................... 128

4.9 Temperature and pressure phase diagram for 25 wt% P85 in D₂O ........................................................... 130

4.10 The zero frequency viscosity for 25 wt% P85 in D₂O along the 207 MPa isobar ..................................................................................... 131

4.11 Microscopic creep data for 35 wt% P85 in H₂O along the 20°C, 58°C, and 68°C isotherms ............................................................ 132

4.12 Zero frequency viscosity for 35 wt% P85 in H₂O as a function of temperature and pressure ........................................................................ 134

4.13 Zero frequency viscosity for 35 wt% P85 in H₂O as a function of temperature and $P - P_c$ ............................................................................. 135

4.14 The normalized transmitted intensity and the estimated inverse osmotic compressibility for 35 wt% P85 in H₂O ......................................................... 137

4.15 Temperature and pressure phase diagram for 35 wt% P85 in H₂O .......................................................... 139

4.16 Microscopic creep data along the 83°C isotherm for 35 wt% P85 in H₂O ......................................................................................... 140
List of Symbols and Notations

\( a \)  
Hydrodynamic radius

\( \alpha \)  
Power-law time scaling of the mean square displacement  
\[(i.e., \alpha = d \ln \langle \Delta r^2(\tau) \rangle / d \ln \tau)\]

\( D_0 \)  
Zero frequency diffusion coefficient  
(or long-time diffusion coefficient)

\( D_{0B} \)  
Zero frequency diffusivity tensor

\( f_B \)  
Stochastic Brownian force

\( G(t) \)  
Stress relaxation modulus

\( G^*(\omega) \)  
Complex modulus, \( G^*(\omega) = G'(\omega) + iG''(\omega) \)

\( G'(\omega) \)  
Storage (or elastic) modulus

\( G''(\omega) \)  
Loss (or viscous) modulus

\( G \)  
Strength of the correlated Brownian force

\( \eta^*(\omega) \)  
Complex viscosity, \( \eta^*(\omega) = \eta'(\omega) + i\eta''(\omega) \)

\( \eta'(\omega) \)  
Dynamic viscosity, or in phase part of the complex viscosity

\( \eta''(\omega) \)  
The out-of-phase component of the complex viscosity

\( \eta_0' \)  
Zero frequency viscosity (or zero shear viscosity), where  
\[\eta_0' = \lim_{\omega \to 0} \eta'(\omega)\]

\( \eta_\infty' \)  
High frequency viscosity, where  
\[\eta_\infty' = \lim_{\omega \to \infty} \eta'(\omega)\]

\( \hat{I} \)  
Identity matrix

\( J_a(\tau) \)  
Microscopic creep compliance  
\[(J_a(\tau) \equiv \left( \pi a / k_B T \right) \langle \Delta r^2(\tau) \rangle)\]

\( J^*(\omega) \)  
Complex compliance, \( J^*(\omega) = J'(\omega) - iJ''(\omega) \)

\( J'(\omega) \)  
Storage (or elastic) compliance

\( J''(\omega) \)  
Loss (or viscous) compliance

\( k_B \)  
Boltzmann constant \((k_B = 1.3806505 \times 10^{-23} \text{ J/K})\)

\( m_p \)  
Mass of the particle

\( m_s \)  
Mass equivalent of the solvent  
\[(\text{mass of the solvent with equal volume of the particle, i.e., } m_s(p_s / p_p) )\]

\( N_A \)  
Avogadro number \((N_A = 6.0221367 \times 10^{23} \text{ 1/mol})\)

\( \bar{p} \)  
Momentum vector

\( \Delta \bar{p}(\tau) \)  
Change in momentum vector  
\[(\Delta \bar{p}(\tau) \equiv \bar{p}(t + \tau) - \bar{p}(t))\]
\( \vec{r} \) Position coordinate

\( \Delta_{\vec{r}}(\tau) \) Displacement vector (\( \Delta_{\vec{r}}(\tau) \equiv \vec{r}(t+\tau) - \vec{r}(t) \))

\( \langle \Delta r^2(\tau) \rangle \) Mean square displacement

\[
\langle \Delta r^2(\tau) \rangle \equiv \langle \Delta_{\vec{r}}(\tau) \cdot \Delta_{\vec{r}}(\tau) \rangle = \langle \text{Tr} \{ \Delta_{\vec{r}}(\tau) \Delta_{\vec{r}}(\tau) \} \rangle
\]

\( \rho_p \) Density of the particle

\( \rho_s \) Density of the solvent

\( \text{Re} \) Reynolds number is defined as the ratio of the inertial to viscous forces (\( \text{Re} = \nu \rho_p / \eta_0 \) for a sphere)

\( \tau_v \) The hydrodynamic time-scale relative to the particle radius

\( (\tau_v = a^2 \rho_p / \eta_s) \)

\( T \) Absolute temperature

\( \langle \vec{v}(t_0) \vec{v}(t_0 + \tau) \rangle \) Velocity Autocorrelation Function (VACF)

\( \zeta \) Friction coefficient

\( \zeta_m \) Specific friction coefficient (i.e., per mass)

\( \langle x \rangle \) The ensemble averaged quantity, or the average over all possible states of the system

\( \langle x \rangle_{\tau} \) The time averaged quantity, where \( \langle x \rangle_{\tau} \equiv \frac{1}{\tau} \int_{t_0}^{t_0+\tau} dt \ x(t) \)

\( \tilde{x} \) The tilde, ~, denotes the unilateral Laplace transform

\[
(\tilde{x} = \mathcal{L}(x) = \int_0^{\infty} dt \ x(t) e^{-st}) \text{ where } s = x + iy
\]

\( \vec{x} \) Single underline denotes a vector

\( x \) Double underline denotes a tensor

\( \hat{x} \) Carrot denotes a vector of unity magnitude

\( \text{Tr}\{\vec{x}\} \) Trace of a square matrix, defined as \( \hat{1} : \vec{x} \) yielding

\[
\text{Tr}\{\vec{x}\} \equiv \sum_{n,m=1}^{N} \hat{1}_{nm}x_{mn} = \sum_{n=1}^{N} x_{nn}
\]

\( \vec{x} \cdot \vec{x} \) Signifies scalar, dot, or inner product

\( \vec{x} \wedge \vec{x} \) Signifies vector, cross, or outer product

\( \vec{xx} \) Signifies tensor, or dyadic product

\( \nabla \) The gradient operator

\( \nabla \cdot \) The divergence operator

\( \nabla \wedge \) The curl operator

\( \nabla^2 \) The Laplacian operator (\( = \nabla \cdot \nabla \))
For almost two decades diffusing wave spectroscopy (DWS) has been used as a method to determine the dynamics of colloidal particles at very small time-scales, on the order of microseconds.\textsuperscript{1-3} This technique has been extended to exploring the frequency dependent response of a complex fluid to thermal perturbations.\textsuperscript{4-6} The standard delta correlated thermal perturbation fluctuation-dissipation theorem is modified to reflect past stochastic events as the energy stored in the fluid structure modifies the mean squared displacement of dispersed probes. Thus, DWS provides unique access to early thermal relaxation modes in a complex fluid, which is the proposed origin of the viscoelastic behavior observed on a macroscopic level.

In this chapter, DWS is introduced by extending the formalism of single scattering to the multiple scattering regime. Using this foundation, an analysis procedure is outlined and further details are provided in the appendices. A description of the experimental methods used in subsequent chapters is presented. Applications of DWS to model systems are then introduced, highlighting the sensitivity of this technique to key physical parameters.

\section*{1.1 PCS to DWS}

The classic dynamic light scattering technique is known as photon correlation spectroscopy (PCS). Light impinges upon a sample and is subsequently scattered owing to dielectric fluctuations of the medium. Time dependent fluctuations of the scattered light are measured, yielding information about the dynamics of the sample. At infinitesimal times the scattered light intensity does not change and remains correlated. After sufficient time has passed, the scattered light intensity will become randomized and reflects molecular level dynamics.

In PCS, photons entering the sample are assumed to only scatter once. In the single scattering limit, the decorrelation of light can be viewed as the Doppler Effect, where the relative motion of the scattering centers is the source of the fluctuating scattered light intensity. Multiple scattering degrades the phase information between scattering events. In the limit of large multiple scattering,
however, the transport of photons can be described as a random walk. Dynamic light scattering in
the multiple scattering limit is called diffusing wave spectroscopy (DWS).2, 7-9

In the following development, the basic concepts of single scattering techniques will be presented and
then extended to the case where a large number of scattering events occur. Photon transport will
then be considered in the multiple scattering continuum limit and modeled with a conservative
equation, specifically the diffusion equation. The experimental geometry and the boundary conditions
ultimately dictate the solution to the diffusion equation and allow for meaningful interpretation of the
intensity fluctuation correlations measured with diffusing wave spectroscopy.

1.1.1 Single Scattering

The development presented here roughly follows that given in references 10 and 11. First, let us
consider a coherent source of photons of wavelength $\lambda$ incident upon a sample of dilute point
scatterers. In such a case the planar electromagnetic field of the light will interact with the samples’s
electrons, and for simplicity, each such interaction can be seen as an oscillating point source that
produces its own spherical electromagnetic field. We shall characterize the incident and scattered
light using the wavevectors, $k_0$ and $k_s$, respectively. Each wavevector points in the direction of the
propagating electromagnetic field with magnitude $2\pi/\lambda$. Both the incident and scattering wavevector
have the same magnitude, and thus the scattering is elastic.

---

* Here I use the notation $k_0$ as the incident wavevector in the medium to be consistent with notation used below; i.e., the “0”
subscript does not indicate the in vacuo value.
For the simple scattering setup given in Figure 1.1, one can focus on two independent scattering events occurring at \( r_1 \) and \( r_2 \). The two photon paths from laser to detector are not the same length. In the diagram, a photon scattering at \( r_2 \) travels a slightly longer distance than a photon scattering at \( r_1 \). The photons will constructively interfere when the total path difference is some integer of the period \( n|k_0| \), where \( n \) is an integer. An expression for the extra distance traveled, \( \Delta \), can be derived as

\[
\Delta = k_0 \frac{E_0}{|E_0|} \cdot (r_2 - r_1) + k_r \frac{E_r}{|E_r|} \cdot (r_1 - r_2) \\
= \frac{\lambda}{2\pi} (k_0 - k_r) \cdot (r_2 - r_1) \\
= -\frac{\lambda}{2\pi} q \cdot (r_2 - r_1) 
\]  

(1.1)

where \( q \equiv k_r - k_0 \), which is sometimes referred to as the momentum transfer, the scattering vector, or simply “\( q \)”. The magnitude of \( q \) can be easily derived and found to be

\[
|q| = \frac{4\pi n s}{\lambda_0} \sin \left( \frac{\theta_s}{2} \right)
\]
where \( n_s \) is the refractive index of the medium and \( \lambda_v \) is the in vacuo wavelength of the incident light. The phase difference between photons from path 1 and photons from path 2 is \( 2\pi\Delta/\lambda \), which from equation (1.1) yields

\[
\Delta \Phi = -q \cdot (\vec{r}_2 - \vec{r}_1).
\]

For the simple case of 2 scattering centers, one can conclude that \( q \) determines the length scale probed in dynamic light scattering. This well-known result confirms that for large length-scales, smaller \( q \) values are required and visa versa. By extending the analysis above to many scattering centers, we find an associated phase,

\[
\Phi_n = -q \cdot \vec{r}_n,
\]

for each scattering center. We now define a scattering center as an independent sub-volume within the scattering medium and the scattered field associated with that volume as

\[
E_{s,n} = \int_{V_{s,n}} d\vec{r} f(\vec{r}) E_0 \exp(-iq \cdot \vec{r})
\]

where \( f(\vec{r}) \) is the scattering strength at point \( \vec{r} \) within the \( n \)th independent scattering sub-volume, \( V_{s,n} \), and is mainly dependent on the dielectric constant of the material relative to that of the medium (see Appendix 1.A). If we define \( f(\vec{r}) \) to be zero when \( \vec{r} \) lies outside the scattering volume, then the total field from all scattering sub-volumes is

\[
E_s = \int_{V_s} d\vec{r} f(\vec{r}) E_0 \exp(-iq \cdot \vec{r}).
\]

To retain the positional information associated with each sub-volume we define the relative position coordinate \( \vec{r}_r' \equiv \vec{r} - \vec{r}_n \) such that \( \vec{r}_n \) is the center of the sub-volume \( V_{s,n} \) and then integrating over each sub-volume

\[
E_s = \sum_{n=1}^{N} \exp\{-iq \cdot \vec{r}_n\} \int_{V_{s,n}} d\vec{r}' f(\vec{r}') E_0 \exp\{-iq \cdot \vec{r}'\}.
\]

The above equation can be interpreted as having an inter-sub-volume contribution from the \( \exp\{-iq \cdot \vec{r}_n\} \) term and an intra-sub-volume contribution from the \( \exp\{-iq \cdot \vec{r}'\} \) term (see Appendix 1.A for a comparison with an expression obtained using Maxwell’s equations).
1.1.2 The Autocorrelation Function and Speckle

In section 1.1.1 we began by analyzing the simple case of two photon interference and then extended the development to multiple photon interference. The constructive and destructive interference of light scattered from many bodies is known as speckle and is illustrated in Figure 1.2.

![Figure 1.2 Hypothetical speckle pattern created from constructive and destructive interference of light scattered within the sample. The black disc represents a pinhole detector.](image)

The positional and geometrical dimensions of the scattering sub-volumes for any given realization dictate the instantaneous speckle pattern. A change in either positional or geometrical dimension yields a different speckle pattern. Therefore speckle is quite dynamic, changing in shape, size, position and intensity. For a colloidal dispersion, such that the dominant scattering contribution is from the suspending particles, the dynamics of the speckle pattern reflects the positional change of the particles.
Sampling the intensity of the speckle pattern at a point yields a signal such as that given below in Figure 1.3.

![Intensity trace at a fixed detector position.](image)

**Figure 1.3 Intensity trace at a fixed detector position.**

As expected, the scattered intensity of randomly moving particles within the sample is also random. However, upon closer examination of the intensity trace the signal appears to be correlated at short times. At these short times, the speckle pattern has not evolved significantly enough to cause a change in intensity at the sampling point. Since the speckle dynamics are directly related to the underlying sample dynamics, the change in intensity at a sampled point reflects changes in the particles’ positions.

The quantity used to characterize the intensity fluctuations is known as the normalized intensity autocorrelation function (IACF).

\[
\begin{align*}
g_2(\tau) &= \frac{\langle i(0)i(\tau) \rangle}{\langle i(0) \rangle^2} \\
\end{align*}
\]

The brackets represent the ensemble average of the intensity fluctuation formally defined as

\[
\langle f \rangle_t = \int d\bar{x}P(\bar{x},t)f(\bar{x}),
\]

where \(P(\bar{x},t)\) is the probability of finding \(f\) in the state \(\bar{f}(\bar{x})\) at time \(t\) and the integral is over all possible states of the system. Experimentally, \(g_2\) is found by taking a time-average and assuming the two quantities are equal, which is the same as stating that the system is ergodic. The validity of ergodicity requires the time-average to be performed over a sufficient time duration such that all possible states will be sampled.
The sample dynamics can be related to the intensity fluctuations within a theoretical description of the scattered electric field. The electric field autocorrelation function (EACF) is related to the intensity autocorrelation function via the Siegert relationship (see Appendix 1.B for details).

\[ g_2(\tau) = 1 + \beta |g_1(\tau)|^2 \]  

(1.5)

The EACF, \(g_i(\tau)\), in expression (1.5) can be related to the underlying system dynamics by inserting equation (1.2) into the definition of the EACF (see equation (1.20) in Appendix 1.B) and assuming isotropic, non-interacting scattering volumes.

\[
g_i(\tau) = \frac{\left\langle \left[ E_s(0) \cdot \hat{n}_n \right] \left[ E^*_s(\tau) \cdot \hat{n}_n \right] \right\rangle}{\left\langle \left[ E_s(0) \cdot \hat{n}_n \right] \left[ E^*_s(0) \cdot \hat{n}_n \right] \right\rangle} = \frac{\left\langle \sum_{n=1}^{N} \exp\left\{-i\mathbf{q} \cdot \mathbf{r}_n(0)\right\} \sum_{n=1}^{N} \exp\left\{i\mathbf{q} \cdot \mathbf{r}_n(\tau)\right\}\right\rangle}{\left\langle \sum_{n=1}^{N} \exp\left\{-i\mathbf{q} \cdot \mathbf{r}_n(0)\right\}\sum_{n=1}^{N} \exp\left\{i\mathbf{q} \cdot \mathbf{r}_n(0)\right\}\right\rangle} \]  

(1.6)

Since we assumed scattering sub-volumes are independent, or more precise, the position of one scattering sub-volume is uncorrelated with another scattering sub-volume, all cross terms become zero, and we have

\[
g_i(\tau) = \frac{\left\langle \sum_{n=1}^{N} \exp\left\{-i\mathbf{q} \cdot \mathbf{r}_n(0) - \mathbf{r}_n(\tau)\right\}\right\rangle}{\left\langle \sum_{n=1}^{N} \exp\left\{-i\mathbf{q} \cdot \mathbf{r}_n(0)\right\}\right\rangle} = \frac{1}{N} \sum_{n=1}^{N} \left\{ \exp\left\{-i\mathbf{q} \cdot \mathbf{r}_n(0) - \mathbf{r}_n(\tau)\right\} \right\} \]  

The bracketed expression above is related to the Fourier transform of the probability of finding a particle at some position \(\mathbf{r}_n\) at some lag time, \(\tau\). The position of a particle undergoing Brownian motion is well described by the Gaussian distribution. Completing the square and taking the Fourier transform gives\(^{12}\)
\[ g_1(\tau) = \frac{1}{N} \sum_{n=1}^{N} \exp \left( -|q|^2 \frac{\langle \Delta r^2(\tau) \rangle}{6} \right) \]

\[ = \exp \left( -|q|^2 \frac{\langle \Delta r^2(\tau) \rangle}{6} \right) \]

where \( \Delta r \equiv r(\tau) - r(0) \). The above expression is related to the long-time diffusion coefficient, as will be demonstrated in the next chapter, yielding

\[ g_1(\tau) = \exp \left( -|q|^2 D_0 \tau \right). \quad (1.7) \]

In general, an autocorrelation function characterizes the time trace of some property that either evolves or fluctuates in time. In the former case, we are often interested in the path that a system takes to attain equilibrium. In the latter case, the system is at or near equilibrium and we are interested in how a local property such as density, fluctuates about its macroscopic value. In either case, the thermal fluctuations reflect the underlying dynamics and in turn the macroscopic properties of a material.

### 1.1.3 From Single to Multiple Scattering

Thus far we have assumed that the majority of photons entering the sample do not scatter and the rest undergo only single scattering events. When multiple scattering occurs the phase information is lost. However, as the number of scattering events becomes sufficiently large we can use statistics to obtain meaningful dynamic information.
Figure 1.4 Description of an arbitrary photon path in random media.

When a photon enters strongly scattering media, it will scatter many times before leaving. We can describe a single photon path, \( n \), as

\[
E_n = \sum_{m=0}^{M} (r_{m+1} - r_m) \cdot \frac{k_m}{k_m}.
\]

(1.8)

where \( r_0 \) and \( r_{M+1} \) are the entrance and exit points of the photon and points \( r_1 \) through \( r_M \) are the various scattering events in the photon path. Given that the speed of light is much greater than the speed of thermal motion, a large number of scattering events will occur for any given particle configuration. Therefore, an ensemble of photon paths is sampled. Similar to the single scattering case, a phase can be associated with a photon path by \( 2\pi s_n / \lambda \), and the total field is given as the sum over all the photon paths

\[
E_x(t) = \sum_{n=1}^{N} E_0(s_n, t) \exp \left\{ \frac{2\pi}{\lambda} s_n(t) \right\}.
\]

(1.9)
This is the multiple scattering equivalent to the single scattering equation (1.2). In both single and multiple scattering, the time-scale is set by how fast the sample decorrelates the scattered laser light. In multiple scattering, however, it is the cumulative effect of all the scatterers’ motion in the photon path that is responsible for the decorrelation of the scattered light. The photon paths are essentially randomized and the concept of a fixed $q$ is no longer applicable. Rather, the dynamical information from multiply scattered light is given over a distribution of photon path-lengths. Furthermore, $E_0$ is not constant and becomes a function of the photon path-length.

The basic approach for constructing the multiple scattering EACF is the same approach as previously done for the single scattering case (see equation 1.6).

$$g_1(\tau) = \left\langle \left| \frac{\langle E_s(0) \cdot \tilde{n} \rangle}{\langle E_s(0) \cdot \tilde{n} \rangle} \right|^2 \right\rangle$$

$$= \left\langle \left\{ \sum_{n=1}^{N} |E(s_n, 0)| \exp \left\{ i \frac{2\pi}{\lambda} s_n(0) \right\} \right\} \left\{ \sum_{n=1}^{N} |E(s_n, \tau)| \exp \left\{ -i \frac{2\pi}{\lambda} s_n(\tau) \right\} \right\} \right\rangle$$

$$= \left\langle \left\{ \sum_{n=1}^{N} \sum_{n' = 1}^{N} |E(s_n, 0)||E(s_{n'}, 0)| \exp \left\{ i \frac{2\pi}{\lambda} [s_n(0) - s_{n'}(0)] \right\} \right\} \right\rangle$$

Since the possible photon paths through the sample are random, the only paths that contribute (i.e., that are correlated) are the self terms, where $n = n'$. Thus, assuming interference effects from photons on different paths are negligible, we find that

$$g_1(\tau) = \left\langle \sum_{n=1}^{N} |E(s_n(0))||E(s_n(\tau))| \exp \left\{ i \frac{2\pi}{\lambda} [s_n(0) - s_{n}(\tau)] \right\} \right\rangle$$

$$= \left\langle \sum_{n=1}^{N} |E(s_n, 0)||E(s_n, \tau)| \exp \left\{ i \frac{2\pi}{\lambda} [s_n(0) - s_{n}(\tau)] \right\} \right\rangle$$

$$= \frac{\sum_{n=1}^{N} \langle |E(s_n, 0)|^2 \rangle}{\sum_{n=1}^{N} \langle |E(s_n, 0)|^2 \rangle} \cdot \frac{\sum_{n=1}^{N} \langle |E(s_n, \tau)|^2 \rangle}{\sum_{n=1}^{N} \langle |E(s_n, 0)|^2 \rangle} \cdot \frac{\sum_{n=1}^{N} \langle |E(s_n, 0)||E(s_n, \tau)| \exp \left\{ i \frac{2\pi}{\lambda} [s_n(0) - s_{n}(\tau)] \right\} \rangle}{\sum_{n=1}^{N} \langle |E(s_n, 0)|^2 \rangle}$$
Defining

\[ P(s_n) \equiv \frac{\langle |E(s_n,0)||E(s_n,\tau)| \rangle}{\sum_{n=1}^{N} \langle |E(s_n,0)|^2 \rangle} \]

which is the fraction of photons taking paths of length \( s_n \) and substituting the expression for the total path-length as the sum of the individual scatterers using equation (1.8) (see Appendix 1.C), the EACF is given by

\[ g_1(\tau) = \sum_{n=1}^{N} P(s_n) \left\{ \exp \left[ i \sum_{m=1}^{M(n)} \Delta \Sigma_m(\tau) \cdot q_m(0) \right] \right\}, \]

where \( \Delta \Sigma_m = \Sigma_m(\tau) - \Sigma_m(0) \) and \( q_m(0) = \xi_m(0) - \xi_{m-1}(0) \). As in the single scattering case, knowing that a particle undergoing Brownian motion is well described by the Gaussian distribution allows us to further simplify the above expression.

\[ \hat{g}_1(\tau) = \sum_{n=1}^{N} P(s_n) \exp \left\{ - \left[ \sum_{m=1}^{M(n)} \Delta \Sigma_m(\tau) \cdot q_m(0) \right] \left[ \sum_{m=1}^{M(n)} \Delta \Sigma_m(\tau) \cdot q_m(0) \right]^* \right\} \]

\[ = \sum_{n=1}^{N} P(s_n) \exp \left\{ - \left[ \sum_{m=1}^{M(n)} \left[ \Delta \Sigma_m(\tau) \cdot q_m(0) \right]^2 \right] \right\} \]

\[ = \sum_{n=1}^{N} P(s_n) \exp \left\{ - M(n) \left\{ \Delta \Sigma(\tau) \cdot q(0) \right\}^2 \right\} \]

\[ = \sum_{n=1}^{N} P(s_n) \exp \left\{ - \frac{M(n)}{6} \left\{ \Delta \Sigma(\tau) \cdot q(0) \right\}^2 \right\} \]

The last step assumes that \( \Delta \Sigma(\tau) \) and \( q(0) \) are uncorrelated. \( M(n) \), the number of scattering events for path \( s_n \), can be written as \( M = s_n/l \), where \( l \) is the scattering mean free path. The average over \( q^2 \), which takes into account the form factor of the particle, \( F(q) \), is

\[ \langle q^2 \rangle = \frac{\int dq |q|^2 F(q)}{\int dq F(q)} = 2k_0^2 \langle 1 - \cos(\theta) \rangle = 2k_0^2 \frac{l^*}{l} \]  

(1.10)

where \( l^* \) is the transport mean free path, which is the characteristic distance the photon must travel before it becomes randomized. Finally, the EACF is expressed as
\[ g_1 (\tau) = \sum_{n=1}^{N} P(s_n) \exp\left\{ -\frac{s_n}{3l^*} k_0^2 \langle \Delta r^2 (\tau) \rangle \right\}, \]

or in the continuum limit

\[ g_1 (\tau) = \int_0^\infty ds P(s) \exp\left\{ -\frac{s}{3l^*} k_0^2 \langle \Delta r^2 (\tau) \rangle \right\}. \]

Equation (1.11) is the central equation connecting the dynamics of the scatterers to the multiple scattering EACF. In the continuum limit \( P(s) \) is the probability that a photon will take a path of length \( s \). The transport mean free path, \( l^* \), can be calculated using Mie theory given the scatterer number density and the refractive indices of the scatterers and medium (Appendix 1.F).

The path-length distribution, \( P(s) \), is determined by assuming that the photons scatter many times before leaving the sample. For a very large number of scattering events the light can be adequately described as diffusing through the sample. The validity of this assumption is conventionally characterized by the ratio of the scattering cell path-length, \( L \), to \( l^* \).\(^\beta\) The value often suggested in literature to satisfy the criteria of diffusing photons is \( L/l^* > 5 \).\(^{11} \) However, as will be shown in section 1.2.2.3, a value of 10 is more realistic. Assuming the validity of the diffusing nature of light, the diffusion equation can be solved and, as will be shown, the mean square displacement can be extracted from the EACF and therefore the IACF.

### 1.1.4 Comparison

In conventional dynamic light scattering experiments multiple scattering is scrupulously avoided because of the complexity in interpreting multiple phase shifting events, resulting in an apparently incoherent signal. When the light begins to multiply scatter the photon scattering path becomes randomized. At the limit of large multiple scattering the paths taken by the ensemble of photons becomes well characterized by a Gaussian distribution. Thus, the photon transport can be accurately described as a diffusing wave. Dynamic light scattering in the multiple scattering limit is called Diffusing Wave Spectroscopy (DWS).

\(^\beta\) It should be noted that the square of this ratio, \((L/l^*)^2\), is probably a better measure since it is approximately the average number of random scattering steps. However, I shall conform to the convention of the simple ratio as being the diffusing approximation measure of validity.
DWS is able to capture dynamics on much shorter length and time scales relative to PCS. The decay of the autocorrelation function in DWS is due to the cumulative motion of each of the scattering particles along the path of the photon. Therefore, DWS gives dynamical information on length-scales as small as a few angstroms\(^8\), whereas PCS is restricted to distances comparable to the wavelength of light.

The advantage of PCS is the overall simplicity of the analysis. Dynamic information is found by simply fitting the decay in the intensity autocorrelation function, which for mono-disperse particles is an exponential (e.g., see equation (1.7)). PCS should be carried out over multiple scattering wavevectors to insure proper scaling of the measured \(D_0\). In comparison, DWS gives dynamical information over a distribution of length scales. However, the DWS analysis is much more complex and its quantitative accuracy is dependent to a greater extent on several independently measured or estimated physical parameters.

In reality, PCS and DWS are not competing techniques in that the scattering limits are incompatible. Samples that are well suited for DWS, by having large multiple scattering, are intractable by PCS methods. Large multiple scattering tends to occur because of a large refractive index mismatch of two species and high scatterer concentrations in the sample. As such, DWS samples are typically strongly scattering colloidal dispersions in nature. This makes the present study of a suspension of particles in complex fluids well suited for DWS measurements.

**1.2 DWS Analysis**

The basic equation used in the interpretation of DWS data was derived earlier as

\[
g_1(t) = \int_0^\infty ds P(s) \exp \left( -\frac{1}{3} k_0^2 \langle \Delta r^2(t) \rangle \frac{s}{l^2} \right). \tag{1.11}
\]

Using the diffusion equation one can find an expression for the distribution of the path-lengths, subject to the boundary conditions specified by the experimental setup, yielding (Appendix 1.D.c)

\[
g_1(\tau) = \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} \int_0^{\infty} d\eta \, d\eta' \, d\eta'' \, d\eta''' \, (1 + C\eta)(1 - C\eta) e^{-2\eta\eta'} e^{-(\eta'^2 - \alpha^2) \frac{d^2}{d\eta^2}} \left( \frac{d^2}{d\eta^2} \right) \left( \frac{d^2}{d\eta'^2} \right) \left( \frac{d^2}{d\eta''^2} \right) \left( \frac{d^2}{d\eta'''^2} \right). \tag{1.12}
\]
In the expression (1.12), $C$ is determined by the boundary conditions (Appendix 1.D.b) and is a function of the scattering cell path-length, $L$, the transport mean free path, $l^*$, and the reflectivity at the sample boundaries. In practice, one obtains a value for the electric field autocorrelation function, $g_1(\tau)$, from the experimentally determined intensity autocorrelation function and then solves equation (1.12) to find the value of $\alpha(\tau)$ in the lower limit of the integral. Thus, to find $\alpha(\tau)$, a root finding algorithm is coupled with numerical integration. For the diffusion equation $\alpha(\tau)$ is related to the mean square displacement by

$$\alpha(\tau) = \left(\frac{L}{l^*}\right)\sqrt{k_0^2 \Delta \tau^2(\tau)}.$$ 

Details on the calculation of $l^*$ and the numerical scheme used to convert $g_1(\tau)$ to $\Delta r^2(\tau)$ can be found in Appendix 1.F and Appendix 1.G, respectively.

### 1.2.1 Experimental Setup

In theory, DWS experiments can be performed at any angle. DWS at large scattering angles shifts the photon path-length distribution towards smaller photon path-lengths. As a result using the diffusion equation to describe this distribution becomes problematic. Regardless, the backscattering geometry is commonly used and has many practical applications such as scattering in human tissue and other optically dense or strongly absorbing media. The transmission geometry in the present studies is preferred due to its overall simplicity. By using the entire thickness of the sample, one can use lower probe concentrations and still achieve multiple scattering, satisfying the diffusion equation. This geometry also allows for straightforward application of boundary conditions. From an experimental point-of-view, the alignment of the optical train is comparatively simple and more easily accommodates a variety of scattering cells. An illustration of the experimental setup is given below in Figure 1.5.

---

\[\text{For the telegrapher equation: } \alpha(\tau) = \frac{L}{\tau} \sqrt{k_0^2 \Delta \tau^2(\tau)} \left[ \frac{k^2 \Delta \tau^2(\tau)}{9} + 1 \right].\]
The first element of the optical train is the laser. In the van Zanten laboratory we employ a Coherent™ diode pumped solid-state (DPSS) continuous wave 532 nm Nd:YAG laser having a maximum power output of 150 mW (Compass 315M). The main advantage of using a DPSS laser is the long coherence length, which is crucial in DWS experiments. The laser light passes through at least one iris and enters the sample where the light multiply scatters. Since the optical train is in transmission geometry there is risk of laser light being back reflected into the laser head. This is minimized by using the first iris and slightly angling all reflective surfaces.

In the solution of the diffusion equation, we assume a point-point geometry, which means the laser light enters the sample as a single point and is detected on axis with that point. The second set of irises following the sample cell helps ensure that only photons on axis are detected and prevents reflected light from re-entering the sample. The light then passes through a polarizer that is rotated 90° relative to the polarization of the laser. This greatly reduces the chance of unscattered photons entering the detector. The light is then collected using a gradient refractive index (GRIN) lens with a very narrow angle of acceptance attached to a 4 axis gimbal. The GRIN lens ensures the validity of the point-point geometry and reduces the effect of stray light. The lens is directly mounted on a single mode optical fiber, which is connected to an ALV™/SI-SIPD photon detector. The photons from the optical fiber are split into two independent photo-multiplier tubes (PMTs) via a beam splitter. The split signal from the ALV™ photon detector is sent to an ALV™ 5000/E digital correlator operating in cross-correlation mode to reduce short-time after pulsing effects.
1.2.1.1 Pressure/Temperature Scattering Cell

The area where the sample is located is wide-open, allowing for a multitude of specially built scattering cells. The primary scattering cell used in this work was originally designed for small angle neutron scattering (SANS) studies over a wide range of temperature and pressure.\textsuperscript{13, 14} The path-length of the scattering cell is 4.58 mm, which is well suited for small-time dynamical investigations of polystyrene dispersions in an aqueous environment.

Figure 1.6 The experimental setup shown here with the high-pressure cell in the optical train. The black box at the right with the yellow cord (optical fiber) is the PMT. The optical train, from left to right, is the GRIN lens, iris, polarizer, iris, scatter cell, iris, 2 neutral density filters, and iris. The laser is off image to the right.

Figure 1.6 showcases the optical train used for the experiments described in this study. The scattering cell is a cylindrical body with four ports allowing access to the sample. In the image below, one can see a thermocouple attached to the top port while the pressure line is connected to the left port. Surrounding the scattering cell is a heating/cooling jacket controlled by a water circulator. The input and output water lines are connected to the jacket on the right. The scattering cell is lined with a Teflon jacket and the windows are ¾ inch thick sapphire. The pressure cell is designed to withstand pressures in excess of 400 MPa.
1.2.2 Experimental Considerations

In the following subsections, several aspects of a typical DWS experiment will be highlighted, specifically those aspects related to the parameters required for extracting the mean square displacement from the intensity autocorrelation function and how inherent errors affect the conversion process. Such analysis in the literature is limited\textsuperscript{15}, and a more comprehensive exploration of the mean square displacement determination will aid in understanding anomalies and the limitations of the DWS technique.

There are at least 8 parameters required to convert the intensity autocorrelation function to meaningful dynamic information. After simple examination of equation (1.11) one can identify the incident wavevector, $\vec{k}_0$, and the transport mean free path, $l^*$. However, to convert the experimentally found intensity autocorrelation function to the electric field autocorrelation function, the data must be fit to the Siegert relationship to find the dynamical contrast, $\beta$. The scattering cell path-length, transport mean free path, and reflectivity at the boundaries are required to properly describe the photon path-length distribution, $P(s)$. The reflectivity is calculated using a three refractive index model where the refractive indices of the medium, scattering cell, and surrounding environment are required. The incident wavevector contains the laser wavelength and the refractive index of the medium. To calculate $P^*$, one must perform a Mie calculation requiring the size and volume fraction of the scatterers as well as the refractive indices of the scatterer and medium. Often the weight fraction, rather than the volume fraction, is known, and an approximation must be made using the medium and scatterer densities. Finally, most of these parameters are sensitive to

Figure 1.7 Image of the high-pressure scattering cell.
temperature and pressure, which is of central importance to the work presented in the following chapters.

In the following subsections, we will focus on the parameters that directly determine the photon path-length distribution, $P(s)$. The most crucial parameter, $l^*$, is the length-scale over which photons become randomized and therefore specifies the breadth of the distribution; this length-scale is normalized by the distance the diffusing photons travel, which is a function of path-length and boundary conditions. Finally, $g_1(\tau)$, as given in equation (1.11), is determined by the Siegert relationship. Analyses of these parameters reveal how systematic errors affect the distribution, thereby affecting the extraction of meaningful dynamic information.

1.2.2.1 The Dynamical Contrast: Fitting the Siegert Relationship

The Siegert relationship given below (also see Appendix 1.B) is used to convert the experimentally determined intensity autocorrelation function into the electric field autocorrelation function. It contains a single fitting parameter, $\beta$,

$$g_2(\tau) = 1 + \beta |g_1(\tau)|^2.$$  

This parameter is known as the dynamical contrast and usually has a value less than 1. The dynamical contrast is a correction factor accounting for an imperfect optical experimental setup, most notably the effect of the pinhole before the detector having a finite size. Using a GRIN lens coupled with a single mode optical fiber, it is possible to greatly minimize stray light and further decrease the detector area, thereby increasing $\beta$. Placing a polarizer before the detector can significantly reduce polarization effects, which deteriorate the quality of $\beta$.

In traditional DLS techniques, such as in PCS, inaccuracies in $\beta$ do not contribute significantly to the error because dynamic information is found by fitting a range of $g_1(\tau)$. In DWS, the mean square displacement is found point-wise, and inaccuracies in the dynamic contrast may lead to a large systematic error at small-times as shown below in Figure 1.8.
Figure 1.8  420 nm spheres diffusing in water at 20°C evaluated using five different values for the dynamical contrast. Fitting the dynamical contrast with a second-order polynomial yields a value of 0.9899.

In Figure 1.8 a single $g_2(\tau)$ data set was converted to the mean square displacement for five different values of the dynamical contrast. The curve generated using a value of 0.9899 for the dynamical contrast was found by fitting a second-order polynomial; this curve also best corresponds to the mean square displacement curve calculated using the diffusivity of 420 nm spheres in water at 20°C. The curvature in the mean square displacement at small-time is due to a self-hydrodynamic effect that will be discussed in the next chapter. The dynamical contrast has the greatest impact on the mean square displacement at short-times. At later times, the dynamic contrast has a negligible effect on the mean square displacement.

1.2.2.2 Diffuse Reflectivity at the Boundary

In order to convert DWS $g_1(\tau)$ data to mean square displacements, the diffusion equation is analytically solved to find the distribution of photon path-lengths arriving at the detector. Early DWS literature used boundary conditions such as a perfectly absorbing boundary, or a zero photon concentration at an extrapolated length outside the sample. The most common practice is to solve
the differential equation by stating that the total flux at the boundary is zero (see Appendix 1.D.b). Often neglected is the reflectivity at the boundary due to the change in refractive index from sample to air, or more accurately, from the sample to the window of the scattering cell to the surrounding air. Oftentimes DWS cells will be placed in a water bath, thereby minimizing this effect. However, one can account for reflectivity at the boundary knowing the index of the medium, the scattering cell window, and the environment.

\[
\langle \Delta r^2(t) \rangle (\text{Å}^2) = \frac{L}{l^*} = 11
\]

Figure 1.9 The effect on the mean square displacement by taking into account reflectivity at the boundary.

In the above figure we see that taking the reflectivity into account results in an overall shift in the mean square displacement trace. This is expected since the result of reflectivity is to keep photons in the sample longer and thereby shifts the path-length distribution to longer path-lengths than predicted without reflectivity. Thus, reflectivity effectively acts as if \(L\) is increased.

1.2.2.3 Errors in the Transport Mean Free Path, \(l^*\)

The first detailed studies of the DWS technique analyzed the intensity autocorrelation function found for a sample of well known viscosity with \(l^*\) as an adjustable parameter.\(^2,3,7\) This sample was then used as a standard for determining the \(l^*\) of other unknown samples using the approximation that the
transmission is proportional to $l^*/L$ in the diffusing limit. It was observed that $l^*$ values found by fitting were on average 7% lower than those calculated using Mie theory. This effect is apparently due to the neglect of the reflectivity at the boundaries. Kaplan et al. derived an expression for the transmission coefficient that included reflectivity:

$$T = \left( \frac{P}{L} \right) \left( \frac{\frac{2}{3} \frac{1 + R}{1 - R} + 1}{\frac{4}{3} \frac{1 + R}{1 - R} + 1} \right)$$  \hspace{1cm} (1.13)$$

where $R$ is the diffuse reflectivity at the boundary. In addition one must also include the reflectivity in the boundary conditions when solving the diffusion equation (see Appendix 1.D.b).

Another issue with comparing the transmissions of a standard and an unknown is that small errors in determining the transmission lead to large errors in the value for $L/l^*$, as shown below in figure Figure 1.10.

![Figure 1.10](image)

Figure 1.10 Equation (1.13) for no reflectivity and reflectivity of a water-sapphire-air boundary.
Clapper et al. showed measured values of transmission versus $L/l^*$ that were in good agreement with theory. However, their data showed a large spread as $L/l^*$ takes on values greater than 1, indicating large experimental error in determining $l^*$ by transmission.

An alternative to the above method is to calculate $l^*$ using Mie theory. From equation (1.10) we find

$$l^* = \frac{l}{1 - \langle \cos(\theta) \rangle}$$

(1.14)

where $\langle \cos(\theta) \rangle$ is known as the asymmetry and is found numerically through a Mie calculation (see Appendix 1.F for computation details). The calculation requires knowledge of the scatterer and medium refractive indices as well as the scatterer size. The scattering mean free path, $l$, is a function of number density and the scattering cross section, which is also calculated from Mie scattering theory. The Mie calculation is most sensitive to the refractive indices. For 420 nm polystyrene spheres in water, a 1% error in the water refractive index leads to a 13% error in $l^*$. Fortunately, using an Abbe refractometer the refractive index is easily measured with an accuracy of about four decimal places.

![Graph](image)

**Figure 1.11** The mean square displacement of 420 nm polystyrene spheres in water determined using an $l^*$ calculated from Mie theory and a 5, 10, 50, and 100% deviation in that value. The viscosity found using $l^*$ of 213 $\mu$m was 0.962 cps, corresponding well to the literature value of 0.968 cps at 21.5°C.
As shown above in Figure 1.11, deviation from the actual $l^*$ results in an overall shift in the mean square displacement. It should be noted that the qualitative temporal scaling of the mean square displacement is preserved for large errors in $l^*$.

1.2.2.4 The Diffusing Approximation: $L/l^*$

The primary assumption of DWS is that the so-called diffusion approximation for light transport is valid. This has been experimentally verified for large values of the path-length to transport mean free path ratio ($L/l^*$). Simple experiments using 10 mm path-length cells where the sphere concentration was increased from 0.1wt% to 1wt% show that $L/l^*$ of 7.4 and greater yield essentially the same mean square displacement, indicating the validity of the diffusion approximation in this regime.\(^\text{11}\)

![Graph](image-url)

**Figure 1.12** The measured mean square displacement of water with various concentrations of spheres corresponding to different $L/l^*$ values. These data suggests that the diffusion approximation requires $L/l^*$ values of $\sim 10$ or larger.

This is also in agreement with reference [17], where they state that experiments with $L/l^*$ less than $\sim 10$ yield a noticeable decrease in the expected time for a photon to travel through a sample, which is attributed to partial ballistic transport. Reference [15] analyzes the deviation in the diffusion approximation by measuring how much $l^*$ changes relative to that of Mie theory. This deviation does
not directly demonstrate any errors in the mean square displacement, since the authors find \( l^* \) by the relative transmission of a sample in comparison with a standard, which in itself is problematic as discussed earlier. The authors do describe their setup well and describe errors due to neglecting boundary reflectivity. As in reference [17], the authors verify that \( L/l^* < 10 \) can lead to a breakdown in the assumptions used in interpreting the correlation function.

A contribution from Lemieux, Vera and Durian\(^{18} \) calls into question the validity of applying the simple diffusion approximation to samples where \( L/l^* \) is less than 20, which they claim is the majority of the samples of interest. The authors instead apply a so-called telegrapher equation, which is capable of including anisotropic scattering and ballistic scattering events (see Appendix 1.D.d). The anisotropy refers to the source distribution of photons being asymmetric and located off center within the scattering medium. The authors claim this analysis allows for accurate interpretation of DWS measurements for samples at \( L/l^* > 5 \). However, considering the data presented in reference [18], a slightly higher \( L/l^* \) value of 8 is probably more realistic.

![Figure 1.13 Comparison of the telegrapher and diffusion equations for \( L/l^* \) less than 12.](image)

Figure 1.13 is a comparison of the same data given in Figure 1.12 for the first three \( L/l^* \) values using the diffusion and the telegrapher equation. One can observe a slight correction however not enough to collapse the \( 4 L/l^* \) data to the rest of the curves. This indicates that either the telegrapher equation is not able to properly account for ballistic photon transport as claimed or that ballistic
transport is not the source of error. There are several other possibilities such as not properly accounting for the anisotropic initial condition or multiple reflections of some photons across the sample.

### 1.2.2.5 Pressure and Temperature Corrections

Several physical parameters are required to calculate the value of $I^s$ using Mie theory. While the scatterer and medium refractive indices have the largest impact on the calculation, the scatterer size and volume fraction are also important. In all the studies presented here, the samples were made gravimetrically using an analytic balance. Therefore, densities are required to calculate the scatterer volume fraction. All these parameters are sensitive to the high hydrostatic pressures considered in the Pluronic P85 work presented in the 4th chapter.

The general strategy is to use measured physical property values when available and approximate values otherwise. The approximate values were found either by multi-parameter models or Taylor series expansions when such models are not available. Below, the effect of poor approximations to physical parameters will be evaluated.

The properties of water are well known over a wide range of temperature and pressure. Multi-parameter models have been developed and are accurate to several significant figures. In the case where the solution properties were not experimentally accessible, deviations from water properties were established as a function of solute concentration. The solution properties were then approximated to exhibit a constant deviation from the water property over the range of the temperatures and pressures considered. For example, the expression used to approximate the refractive index is given as

$$n_{\text{soln}}(T, P) = n_{\text{water}}(T, P) + \left(\frac{dn}{dc}\right)_c c.$$  

In the case of the probe particles, all physical parameters were found for polystyrene at a reference temperature and pressure and then estimated to the first order using a Taylor series expansion such as

$$\rho = \rho_0 + \frac{d\rho}{dT}(T - T_0) \left(1 + \frac{\rho}{B}\right) \quad \text{and} \quad n = n_0 + \frac{dn}{dT} \frac{dP}{d\rho}(\rho - \rho_0)$$

where the parameters $\rho_0 = 1.051$ g/cm$^3$, $n_0 = 1.598$, $B = 6.59 \times 10^5$ psia, $d\rho/dT \sim -2.65 \times 10^{-4}$ g/cm$^3$K, and $dn/dT \sim -1.42 \times 10^{-4}$ 1/K were found in the Polymer Handbook.
In the table below, we evaluate the effect of changing temperature and pressure for a system of 1 wt% 420 nm polystyrene spheres in water. It is interesting to note that pressure and temperature have little effect on the Mie calculation of \( l^* \). As a result, the expected inaccuracies of the linear approximations mentioned above are presumed to have a minor impact.

### Table 1.1 The physical parameters for a 1 wt% 420 nm polystyrene spheres in water estimated using the multi-parameter model for water\(^ {19,20} \) and the approximations for polystyrene mentioned above.

<table>
<thead>
<tr>
<th>( T ) (°C)</th>
<th>( P ) (MPa)</th>
<th>( n_{\text{water}} )</th>
<th>( \rho_{\text{water}} ) (g/cm(^3))</th>
<th>( n_{\text{PS}} )</th>
<th>( \rho_{\text{PS}} ) (g/cm(^3))</th>
<th>( \phi_{\text{PS}} )</th>
<th>( r_{\text{PS}} ) (nm)</th>
<th>( l^* ) (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0</td>
<td>1.3354</td>
<td>0.9982</td>
<td>1.5982</td>
<td>1.051</td>
<td>0.095</td>
<td>420</td>
<td>213</td>
</tr>
<tr>
<td>80</td>
<td>0</td>
<td>1.3253</td>
<td>0.9718</td>
<td>1.5897</td>
<td>1.035</td>
<td>0.0939</td>
<td>422</td>
<td>211</td>
</tr>
<tr>
<td>80</td>
<td>240</td>
<td>1.3643</td>
<td>1.0872</td>
<td>1.6298</td>
<td>1.11</td>
<td>0.0979</td>
<td>412</td>
<td>207</td>
</tr>
</tbody>
</table>

### 1.2.3 Summary

Two categories of systematic errors have been recognized. The first type affects specific regions of the data. When the diffusing approximation of photon transport breaks down, the mean square displacement at larger time-scales is more susceptible to error since photons scatter fewer times. Results for \( L/l^* > 10 \) indicate that photons entering the sample do undergo diffusive behavior. A poor approximation of the dynamical contrast found in the Siegert relationship results in a mean square displacement trace becoming systematically worse at small time-scales. However, analyzing the intensity autocorrelation function with a simple second order polynomial for a model system of polystyrene spheres in water allowed for accurate temporal scaling at early time-scales.

The second type of systematic error preserves the scaling of the data but shifts the entire curve, degrading the quantitative accuracy. Physical parameters encompassed in the value of \( l^* \) appear to only affect the qualitative behavior of the mean square displacement. The sensitivity of physical parameters to temperature and pressure does not manifest itself in \( l^* \) sensitivity. Although such adjustments will be carried out in the following studies, we can proceed forth with confidence that inaccuracies in such approximations will not adversely affect the results and more importantly their interpretation.
Appendix 1.A  Maxwell’s Equations

The expression for the scattered electromagnetic field derived above (equation (1.2)) contains the essential elements to describe interference effects that lead to a scattering description of the fluid structure. A more careful derivation would begin with Maxwell’s equations to describe the transport of light. For completeness and comparison we present the following expression obtained using Maxwell’s equations in the far field limit\(^{10}\)

\[
E_s(r, q) = \frac{k_0^2}{4\pi} \exp\{i|k_0||\mathbf{r}|\} \left[\mathbf{I} - \hat{k}_s \hat{k}_s\right] \cdot \sum_{n=1}^{N} \exp\{-iq \cdot \mathbf{r}_n\} \left[\int_{V_{n,\alpha}} d\mathbf{r}' \frac{\varepsilon(\mathbf{r}') - \varepsilon_f}{\varepsilon_f} \exp\{-iq' \cdot \mathbf{r}'\}\right] \cdot E_0
\]

(1.15)

Here \(\varepsilon(\mathbf{r})\) is the dielectric constant at \(\mathbf{r}\), \(\mathbf{I}\) is the identity matrix, the dyadic product, \(\hat{k}_s \hat{k}_s\), defines the orientation of the scattered field, and \(\varepsilon_f\) is the dielectric constant for an isotropic medium. The main difference in this formulation compared to equation (1.2) is the tensorial nature of light is retained. This is of major importance if the dominant scattering sub-volumes have an anisotropic component to their geometric shape or the dielectric constant. By comparison with equation (1.2) we find that the scattering strength for isotropic scattering is

\[
f(r) = \frac{\varepsilon(\mathbf{r}) - \varepsilon_f}{\varepsilon_f}.
\]

The prefactor of order \(\exp\{i|k_0||\mathbf{r}|/|\mathbf{r}|\}\) in Equation (1.15) reflects the conservation of energy inherent to Maxwell’s equations. That is, equation (1.2) was not formulated to account for the scattered field weakening as a spherical wave; instead, it was based on the conservation of only those photons incident upon the sample, scattering at angle \(\theta_s\), and finally interfering as a plane wave. It is intuitive that the detected field will weaken as the distance from sample increases, a fact not predicted by equation (1.2). However, the functional part of the equation that we are interested in (i.e., the relative distances) is the same in either equation. In fact, this prefactor is not needed in our earlier expression for dynamic measurements, and is lumped together into a calibration constant for static measurements.
Appendix 1.B  Intensity Autocorrelation Function and the Siegert Relationship

From the observation that correlated intensity leads to dynamical information we define the quantity

\[ G_2(\tau) \equiv \langle i(t) i(t + \tau) \rangle \]

as the non-normalized intensity autocorrelation function, where the angular brackets indicate an ensemble average. Experimentally, we perform an average over time and assume that it is the same as the ensemble average, which is equivalent to the assumption that our sample is ergodic. Ergodicity is expected to apply as long as the sample dynamics do not change over time. Furthermore, ergodicity requires a large number of independent realizations so that we can say the autocorrelation function statistically represents the entire system. Thus, ergodicity also implies that the intensity autocorrelation function is only dependent upon the delay time and not the initial time. Hence, \( G_2(\tau) \) is only a function of \( \tau \), i.e.,

\[ G_2(\tau) = \langle i(0) i(\tau) \rangle \quad (1.16) \]

The scattered intensity is the experimentally realizable measurement of the electric field as

\[ i(t) = \frac{1}{2} \sqrt{\frac{\varepsilon_f}{\mu_0}} (E_s(t) \cdot \hat{n}_s)(E_s^*(t) \cdot \hat{n}_s) \quad (1.17) \]

where \( \varepsilon_f \) is the dielectric constant of the medium, \( \mu_0 \) is the magnetic permittivity in a vacuum, \( \hat{n}_s \) is the polarization at the detector and * indicates complex conjugation. Applying equation (1.17) to equation (1.16) we get an expression for the intensity autocorrelation function in terms of the electric field.

\[ G_2(\tau) = \frac{1}{4 \mu_0} \langle [E_s(0) \cdot \hat{n}_s][E_s^*(0) \cdot \hat{n}_s][E_s(\tau) \cdot \hat{n}_s][E_s^*(\tau) \cdot \hat{n}_s] \rangle \quad (1.18) \]

Given that the scattered electric field is a random variable measured over many independent realizations we can assert, with the aid of the central limit theorem, that the electric field is a Gaussian distributed quantity. As such we can use Wicks theorem to write equation (1.18) as\(^{10}\)
\[ G_2(\tau) = \frac{1}{4 \mu_0} \varepsilon_f \]

\[ \langle [E_0(0) \cdot \hat{n}_s] [E_0^\dagger(0) \cdot \hat{n}_s] \rangle \langle [E_\tau(\tau) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle \]
\[ + \langle [E_0(0) \cdot \hat{n}_s] [E_\tau(\tau) \cdot \hat{n}_s] \rangle \langle [E_0^\dagger(0) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle \]
\[ + \langle [E_0(0) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle \langle [E_0^\dagger(0) \cdot \hat{n}_s] [E_\tau(\tau) \cdot \hat{n}_s] \rangle \]

The first term is the self correlation of the electric field and is the average intensity of the scattered field

\[ \langle i(0) \rangle^2 = \langle i(0) \rangle \langle i(\tau) \rangle = \frac{1}{4 \mu_0} \varepsilon_f \langle [E_0(0) \cdot \hat{n}_s] [E_0^\dagger(0) \cdot \hat{n}_s] \rangle \langle [E_\tau(\tau) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle \]

The second term is zero for all \( q \) not equal to zero. Finally we define the quantity

\[ G_1(\tau) = \frac{1}{2} \sqrt{\varepsilon_f} \langle [E_0(0) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle \]

as the non-normalized electric field autocorrelation function. We now write equation (1.18) as

\[ G_2(\tau) = \langle i(0) \rangle^2 + |G_1(\tau)|^2. \]

Further defining the normalized intensity autocorrelation function as

\[ g_2(\tau) \equiv \frac{G_2(\tau)}{\langle i(0) \rangle^2} \]
\[ = \frac{\langle i(0) i(\tau) \rangle}{\langle i(0) \rangle^2} \]
\[ = \frac{\langle [E_0(0) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] [E_0^\dagger(0) \cdot \hat{n}_s] [E_\tau(\tau) \cdot \hat{n}_s] \rangle}{\langle [E_0(0) \cdot \hat{n}_s] [E_0^\dagger(0) \cdot \hat{n}_s] \rangle^2} \]

and the normalized electric field autocorrelation function as

\[ g_1(\tau) \equiv \frac{G_1(\tau)}{\langle i(0) \rangle} = \frac{\langle [E_0(0) \cdot \hat{n}_s] [E_\tau^\dagger(\tau) \cdot \hat{n}_s] \rangle}{\langle [E_0(0) \cdot \hat{n}_s] [E_0^\dagger(0) \cdot \hat{n}_s] \rangle} \]

yields the so-called Siegert relationship

\[ g_2(\tau) = 1 + |g_1(\tau)|^2. \]
By definition (see equations (1.19) & (1.20)) \( g_2(\tau \to 0) \to 2 \) and \( g_1(\tau \to 0) \to 1 \). The normalized intensity autocorrelation function has a nice interpretation that when the quantity \( i(0) \) and \( i(\tau) \) become independent, or uncorrelated, the quantity \( \langle i(0)i(\tau) \rangle \) becomes \( \langle i(0)i(\tau) \rangle = (i(0))^2 \) and thus \( g_2(\tau) \to 1 \). Therefore, \( g_1 \in [0,1] \) and \( g_2 \in [1,2] \).

Experimentally, the limit of \( g_2^{\text{expt}}(\tau) \) as \( \tau \) goes to zero turns out to be a value less than 1. This is primarily due to the size of the speckle relative to the size of the detector pinhole. As the size of the pinhole increases, more than one speckle will be sampled at the same time. As the pinhole size is further increased, several speckles are simultaneously sampled such that average intensity is measured and in such a case \( g_2(\tau) \to 1 \) for all \( \tau \). In general, the Siegert relationship can be modified as

\[
g_2(\tau) = 1 + \beta |g_1(\tau)|^2
\]

where \( \beta \) or the so-called dynamical contrast and is determined experimentally from

\[
\beta = \lim_{\tau \to 0} g_2(\tau).
\]

**Appendix 1.C Multiple Scattering Phase Difference**

The phase difference for a photon on path \( s_n \) after time, \( \tau \), has elapsed is

\[
\frac{2\pi}{\lambda} [s_n(0) - s_n(\tau)] = \sum_{m=0}^{M} [\tau_{m+1}(\tau) - \tau_m(\tau)] \cdot \hat{k}_m(\tau) - \sum_{m=0}^{M} [\tau_{m+1}(0) - \tau_m(0)] \cdot \hat{k}_m(0).
\]

Re-indexing and rearranging the right-hand side yields

\[
\text{R.H.S.} = \sum_{m=0}^{M} [\tau_{m+1}(\tau) \cdot \hat{k}_m(\tau) - \tau_m(\tau) \cdot \hat{k}_m(\tau)] - \sum_{m=0}^{M} [\tau_{m+1}(0) \cdot \hat{k}_m(0) - \tau_m(0) \cdot \hat{k}_m(0)]
\]

\[
= \sum_{m=0}^{M} [\tau_{m+1}(\tau) \cdot \hat{k}_m(\tau) - \tau_{m+1}(0) \cdot \hat{k}_m(0)] - \sum_{m=0}^{M} [\tau_m(\tau) \cdot \hat{k}_m(\tau) - \tau_m(0) \cdot \hat{k}_m(0)]
\]

\[
= \sum_{m=0}^{M} [\tau_m(\tau) \cdot \hat{k}_{m-1}(\tau) - \tau_m(0) \cdot \hat{k}_{m-1}(0)] - \sum_{m=0}^{M} [\tau_m(\tau) \cdot \hat{k}_m(\tau) - \tau_m(0) \cdot \hat{k}_m(0)]
\]

\[
= \sum_{m=1}^{M} [\tau_m(\tau) \cdot \hat{k}_{m-1}(\tau) - \tau_m(0) \cdot \hat{k}_{m-1}(0)] - \sum_{m=1}^{M} [\tau_m(\tau) \cdot \hat{k}_m(\tau) - \tau_m(0) \cdot \hat{k}_m(0)]
\]

\[
+ [\tau_{M+1}(\tau) \cdot \hat{k}_M(\tau) - \tau_{M+1}(0) \cdot \hat{k}_M(0)] - [\tau_0(\tau) \cdot \hat{k}_0(\tau) - \tau_0(0) \cdot \hat{k}_0(0)]
\]
The last two terms are related to the position of the source and the detector which are stationary and thus \( S_{M+1}(0) = S_{M+1}(\tau), S_0(0) = S_0(\tau) \), \( k_M(\tau) = k_M(0) \), and \( k_0(\tau) = k_0(0) \) yielding

\[
\text{Last Two Terms} = S_{M+1}(t) \cdot [k_M(\tau) - k_M(0)] - S_0(t) \cdot [k_0(\tau) - k_0(0)] = 0
\]

Defining

\[
q_m(t) \equiv k_m(t) - k_{m-1}(t)
\]

and simplifying

\[
\text{R.H.S.} = \sum_{m=1}^{M} [S_m(\tau) \cdot k_{m-1}(\tau) - S_m(0) \cdot k_{m-1}(0)] - \sum_{m=1}^{M} [S_m(\tau) \cdot k_m(\tau) - S_m(0) \cdot k_m(0)]
\]

\[
= \sum_{m=1}^{M} S_m(\tau) \cdot [k_{m-1}(\tau) - k_{m}(\tau)] - S_m(0) \cdot [k_{m-1}(0) - k_{m}(0)]
\]

\[
= \sum_{m=1}^{M} S_m(\tau) \cdot q_m(\tau) - S_m(0) \cdot q_m(0)
\]

Thus one can generally write

\[
\Delta \phi_m(\tau) = -\Sigma[\Delta(\tau \cdot q)]
\]

where \( \Sigma[\Delta(\tau \cdot q)] \) represents the phase change of a photon on path \( n \) at time, \( t \), to time, \( t + \tau \). To state it another way, \( \Sigma[\Delta(\tau \cdot q)] \) represents the change in the \( n^{th} \) path-length due to the positional change of all scatterers on path \( n \) over time. Considering the positional change of each scatterer leads to further simplification

\[
\text{R.H.S.} = \sum_{m=1}^{M} [S_m(\tau) \cdot k_{m-1}(\tau) - S_m(\tau) \cdot k_m(\tau)] - [S_m(0) \cdot k_{m-1}(0) - S_m(0) \cdot k_m(0)].
\]

Defining \( \Delta k_m \equiv k_m(\tau) - k_m(0) \), we write \( q_m(\tau) \) as

\[
q_m(\tau) = k_m(\tau) - k_{m-1}(\tau)
= k_m(0) - \Delta k_m - k_{m-1}(0) + \Delta k_{m-1}
= q_m(0) - \Delta k_m + \Delta k_{m-1}
\]

\[
\text{R.H.S.} = -\sum_{m=1}^{M} S_m(\tau) \cdot \left[ q_m(0) - \Delta k_m + \Delta k_{m-1} \right] - S_m(0) \cdot q_m(0)
\]
and defining $\Delta r_m \equiv r_m(\tau) - r_m(0)$ we have

$$R.H.S. = -\sum_{m=1}^{M} \tau_m(\tau) \cdot \left[ q_m(0) - \Delta k_m + \Delta k_{m-1} \right] - \left[ \sum_{m=1}^{M} \tau_m(\tau) - \Delta r_m \right] \cdot q_m(0)$$

$$= -\sum_{m=1}^{M} \tau_m(\tau) \cdot \left[ -\Delta k_m + \Delta k_{m-1} \right] - \Delta r_m \cdot q_m(0) \quad \text{(1.21)}$$

$$= \sum_{m=1}^{M} \Delta r_m \cdot q_m(0) + \sum_{m=1}^{M} \tau_m(\tau) \cdot \left[ \Delta k_m - \Delta k_{m-1} \right]$$

The second term in equation (1.21) is the sum over the difference of the random variables, $\Delta k_m$ and $\Delta k_{m-1}$, which tends to zero for sufficiently large $M$. Therefore, the phase difference for a photon on path $s_n$ over the lag time, $\tau$, is entirely accounted for by the individual scatterer displacements.

$$\frac{2\pi}{\lambda} [s_n(0) - s_n(\tau)] \approx \left[ \sum_{m=1}^{M} \Delta r_m \cdot q_m(0) \right]_n \quad \text{(1.22)}$$

**Appendix 1.D The Diffusion Equation**

In its simplest form the diffusion equation is written as

$$\frac{\partial \varphi}{\partial t} = D_l \nabla^2 \varphi \quad \text{(1.23)}$$

where for the case of light diffusion, $\varphi$ is the energy density of light. The diffusion coefficient of the light, $D_l$, can be written as $c l^* / 3$, where $l^*$ is the transport mean free path and $c$ is the speed of light in the medium. The distance that a photon has traveled in the sample can be simply related to the residence time of the photon in the sample. We can then write equation (1.23) in terms of path-lengths of the sample given $s = ct$.

$$\frac{\partial \varphi}{\partial s} = D^* L \nabla^2 \varphi \quad \text{(1.24)}$$

where $D^* = l^*/3L$ and $L$ is some characteristic length-scale typically defined by the sample geometry such as the path-length of the scattering cell.
Appendix 1.D.a  Initial Conditions

Regarding the initial condition, or position, we model the emergence of photons as a point source.

\[ \varphi(r, s = 0) = \varphi_0 \delta(r - r_p, s) \]  

(1.25)

As will be demonstrated, we shall use the method of Green’s functions to solve equation (1.24), and as such, a more accurate expression for the initial condition can be simply introduced if the distribution of the source is known.

Appendix 1.D.b  Boundary Conditions

At the boundary we write that the total flux of the light must be zero. To find the total light flux the local light flux must integrated over all angles.

\[
\text{Figure 1.14 Scattering geometry used to calculated the photon flux (adapted from reference 22).}
\]

The flux of photons from volume \(dV\) passing through surface \(dS\) is given by the product of the number of photons generated at \(dV\) and the fractional solid angle \((\cos(\phi)dS/4\pi r^2)\), the speed of light, and the loss due to scattering between \(dV\) and \(dS\) \((\exp(-r/l))\) yielding\(^5\)

\(^5\) \(\pi\) corresponds the solid angle of all subtended space, thus we divide by \(4\pi\) to find the fractional solid angle.
\[
\varphi(r, \theta, \phi) \, dV \, e^{\frac{\cos(\phi) \, dS}{4\pi r^2}} e^{-r\mathbb{I}}
\]

Replacing \(dV\) with \(r^2 \sin(\phi) \, dr \, d\theta \, d\phi\) we have

\[
\frac{dS}{4\pi} e^{\varphi(r, \theta, \phi) \sin(\phi) \cos(\phi) e^{-r\mathbb{I}} \, dr \, d\theta \, d\phi}
\]

The total flux into the top of \(dS\) can then be expressed by integrating over the top hemisphere (i.e., the flux of photons is coming from negative \(z\) direction) as

\[
J_- dS = \frac{dS}{4\pi} e^{\varphi(r, \theta, \phi) \cos(\phi) \sin(\phi) e^{-r\mathbb{I}}}. 
\quad \text{(1.26)}
\]

Since the scattered light tends to be a few mean free paths away, we expand the energy density to first order in Cartesian coordinates as

\[
\varphi(r, \theta, \phi) = \varphi_0 + \varphi_0 \left( \frac{\partial \varphi}{\partial x} \right)_0 + y \left( \frac{\partial \varphi}{\partial y} \right)_0 + z \left( \frac{\partial \varphi}{\partial z} \right)_0
\]

and in polar coordinates as

\[
\varphi(r, \theta, \phi) = \varphi_0 + r \cos(\theta) \sin(\phi) \left( \frac{\partial \varphi}{\partial x} \right)_0 + r \sin(\theta) \sin(\phi) \left( \frac{\partial \varphi}{\partial y} \right)_0 + r \cos(\phi) \left( \frac{\partial \varphi}{\partial z} \right)_0.
\]

Since the integration over \(\theta\) in equation (1.26) is from 0 to \(2\pi\) several terms are eliminated (i.e., terms with \(\theta\) do not contribute) and we then write

\[
J_- = \frac{1}{4\pi} e^{\int_{0}^{\pi/2} \int_{0}^{2\pi} \int_{0}^{\infty} dr \left[ \varphi_0 + r \cos(\phi) \left( \frac{\partial \varphi}{\partial z} \right)_0 \right] \cos(\phi) \sin(\phi) e^{-r\mathbb{I}}}
\]

\[
J_- = \frac{1}{4\pi} e^{\int_{0}^{\pi/2} \int_{0}^{2\pi} \int_{0}^{\infty} dr \left[ \varphi_0 \cos(\phi) \sin(\phi) + I^2 \cos^2(\phi) \sin(\phi) \left( \frac{\partial \varphi}{\partial z} \right)_0 \right]}
\]

\[
J_- = \frac{1}{2} e^{\int_{0}^{\pi/2} \int_{0}^{2\pi} \varphi_0 \cos(\phi) \sin(\phi) + I^2 \cos^2(\phi) \sin(\phi) \left( \frac{\partial \varphi}{\partial z} \right)_0}
\]
\[ J_- = \frac{1}{4} c l \varphi_0 + \frac{1}{6} c l^2 \left( \frac{\partial \varphi}{\partial z} \right)_0 \]

If we repeat this analysis for photons that go into \( dS \) from the positive direction we have

\[ J_+ = \frac{1}{4} c l \varphi_0 - \frac{1}{6} c l^2 \left( \frac{\partial \varphi}{\partial z} \right)_0 \]

To generalize from isotropic to anisotropic we can simply substitute \( l \rightarrow l^* \). Assuming no reflectivity at the boundary, we say that there is no net flux into the sample (\( i.e., J_+ = 0 \) at \( z = 0 \) and \( J_- = 0 \) at \( z = L \))

\[ \varphi + l^* \frac{2}{3} \frac{\partial \varphi}{\partial z} = 0 \text{ at } z = 0 \]
\[ \varphi - l^* \frac{2}{3} \frac{\partial \varphi}{\partial z} = 0 \text{ at } z = L \]

This inherently implies that light is generated from within the sample, which is consistent with the initial boundary condition. More generally we can write

\[ \varphi + l^* \frac{2}{3} \hat{n} \cdot \nabla \varphi = 0 \]

at the boundaries. By adding reflectivity we are essentially saying that a certain fraction of the light that would normally exit is entering or being returned to the volume. This implies that

\[ J_+ = RJ_- \text{ at } z = 0 \]
\[ J_- = RJ_+ \text{ at } z = L \]

Thus, at \( \zeta = 0 \)

\[ \left[ \frac{1}{4} c l^* \varphi_0 - \frac{1}{6} c l^2 \left( \frac{\partial \varphi}{\partial z} \right)_0 \right] = R \left[ \frac{1}{4} c l^* \varphi_0 + \frac{1}{6} c l^2 \left( \frac{\partial \varphi}{\partial z} \right)_0 \right] \]

\[ 0 = \varphi_0 (1 - R) - \frac{2}{3} l^* \left( \frac{\partial \varphi}{\partial z} \right)_0 (1 + R) \]
\[ 0 = \varphi_0 - \kappa \left( \frac{\partial \varphi}{\partial z} \right)_0 \text{ where } \kappa \equiv l^* \frac{2}{3} \frac{(1 + R)}{(1 - R)} \]
and likewise at $\zeta = L$

$$0 = \varphi_0 + \kappa \left( \frac{\partial \varphi}{\partial z} \right)_0 \text{ where } \kappa \equiv \frac{2 (1 + R)}{3 (1 - R)}$$

Assuming all boundaries have the same reflectivity

$$\varphi + \kappa \hat{n} \cdot \nabla \varphi = 0$$

If $t$ is the residence time of a photon in the sample, then $s$ is the total path-length of that photon, where $s = ct$. Thus, the distribution of path-lengths, $P(s)$, is proportional to the flux leaving the sample at time $t$. From Ficks law

$$P(s) \propto \left| J_{Lz} \right| = D \left| \hat{n} \cdot \nabla \varphi \right|_{z=L}$$

### Appendix 1.D.c The Solution to the Diffusion Equation in Cylindrical Coordinates

Equation (1.23) in cylindrical coordinates is written as

$$\frac{\partial^2 \varphi}{\partial r^2} + \frac{1}{r} \frac{\partial \varphi}{\partial r} + \frac{\partial^2 \varphi}{\partial z^2} - \frac{c}{D} \frac{\partial \varphi}{\partial s} = 0$$

(1.27)

Subject to the following initial and boundary conditions (see previous section)

$$\varphi(s = 0, r, z) = \varphi_0 \delta(s, r, z - z_0)$$

(1.28)

$$0 = \varphi - \kappa \left( \frac{\partial \varphi}{\partial z} \right) \text{ at } z = 0$$

(1.29)

$$0 = \varphi + \kappa \left( \frac{\partial \varphi}{\partial z} \right) \text{ at } z = L$$

Multiplying equation (1.27) by $L^2$ yields

$$\frac{\partial^2 \varphi}{\partial \ell^2} + \frac{1}{\ell} \frac{\partial \varphi}{\partial \ell} + \frac{\partial^2 \varphi}{\partial \zeta^2} - \frac{L}{D'} \frac{\partial \varphi}{\partial s} = 0$$

(1.27)

where $\ell = r/L$, $\zeta = z/L$ and $D' = \ell / 3L$. Following Laplace transformation
\[ \frac{\partial^2 \varphi}{\partial \ell^2} + \frac{1}{\ell} \frac{\partial \varphi}{\partial \ell} + \frac{\partial^2 \varphi}{\partial \zeta^2} - \frac{L}{D^*} \varphi = -\frac{L}{D^*} \varphi(0) \]

where \( \varphi(0) = \varphi(0, r, z) = \lim_{p \to 0} \varphi_0 \delta(p) \delta(\ell) \delta(\zeta - \zeta_0) \). Greens's function techniques can be used to solve the differential equation (pg 372, §14.10 Carslaw & Jaeger) and with \( \alpha^2 \equiv \frac{Lp}{D^*} \) the solution is

\[ \varphi = \frac{L}{4\pi D^*} \int_0^\infty d\xi \int_0^\infty \frac{\xi}{\eta} J_0(\xi\ell)[\varphi_0 e^{-\eta^2 - \xi^2} + A \sinh(\eta \zeta) + B \sinh(\eta[1 - \zeta])] \] 

(1.30)

where \( \ell \) is the dimensionless distance of the point source from the axis of symmetry and \( \eta^2 \equiv \xi^2 + \alpha^2 \). The constants can be found using the dimensionless form of the boundary conditions (1.29)

\[ \varphi - C \frac{\partial \varphi}{\partial \zeta} = 0 \text{ at } \zeta = 0 \]
\[ \varphi + C \frac{\partial \varphi}{\partial \zeta} = 0 \text{ at } \zeta = 1 \] 

(1.31)

where \( C \equiv \kappa/L \).

For \( \zeta = 0 \)

\[ 0 = \frac{L}{4\pi D^*} \int_0^\infty d\xi \int_0^\infty \frac{\xi}{\eta} J_0(\xi\ell)[\varphi_0 e^{\eta(\xi - \eta \zeta_0)} + A \sinh(\eta \zeta) + B \sinh(\eta[1 - \zeta])] \]

\[ - \frac{L}{4\pi D^*} \int_0^\infty d\xi \int_0^\infty \frac{\xi}{\eta} J_0(\xi\ell)[C\varphi_0 e^{\eta(\xi - \eta \zeta_0)} + AC \eta \cosh(\eta \zeta) - BC \eta \cosh(\eta[1 - \zeta])] \]

\[ = \frac{L}{4\pi D^*} \int_0^\infty d\xi \int_0^\infty \frac{\xi}{\eta} J_0(\xi\ell) \left\{ \varphi_0 e^{\eta(\xi - \eta \zeta_0)}(1 - C\eta) + A[\sinh(\eta \zeta) - C\eta \cosh(\eta \zeta)] + B[\sinh(\eta[1 - \zeta]) + C\eta \cosh(\eta[1 - \zeta])] \right\} \]

\[ = \frac{L}{4\pi D^*} \int_0^\infty d\xi \int_0^\infty \frac{\xi}{\eta} J_0(\xi\ell) \left\{ \varphi_0 e^{\eta(\xi - \eta \zeta_0)}(1 - C\eta) - AC \eta + B[\sinh(\eta) + C\eta \cosh(\eta)] \right\} \]
For $\zeta = 1$

\[
0 = \frac{L}{4\pi D^2} \int_0^\infty d\xi \xi J_0(\xi \ell) \left[ \varphi_0 e^{-\eta(1-\zeta)} + A \sinh(\eta \zeta) + B \sinh(\eta[1-\zeta]) \right] \\
+ \frac{L}{4\pi D^2} \int_0^\infty d\xi \xi J_0(\xi \ell) \left[ -C \eta \varphi_0 e^{-\eta(1-\zeta)} + A C \eta \cosh(\eta \zeta) - B C \eta \cosh(\eta[1-\zeta]) \right] \\
= \frac{L}{4\pi D^2} \int_0^\infty d\xi \xi J_0(\xi \ell) \left\{ -\varphi_0 e^{-\eta(1-\zeta)} (1 - C \eta) + A [\sinh(\eta \zeta) + C \eta \cosh(\eta \zeta)] \\
+ B [\sinh(\eta[1-\zeta]) - C \eta \cosh(\eta[1-\zeta])] \right\} \\
= \frac{L}{4\pi D^2} \int_0^\infty d\xi \xi J_0(\xi \ell) \left\{ -\varphi_0 e^{-\eta(1-\zeta)} (1 - C \eta) + A [\sinh(\eta) + C \eta \cosh(\eta)] - B C \eta \right\}
\]

Given that if the integrand is zero then the integral must also be zero (Raymond-duBois Lemma) we have

\[
0 = \varphi_0 e^{-\eta \zeta} (1 - C \eta) - A C \eta + B [\sinh(\eta) + C \eta \cosh(\eta)] \\
0 = -\varphi_0 e^{-\eta(1-\zeta)} (1 - C \eta) + A [\sinh(\eta) + C \eta \cosh(\eta)] - B C \eta
\]

where $A$ and $B$ are found following extensive algebra

\[
A = \frac{\varphi_0 e^{-\eta(1+\zeta)}}{(C \eta - 1) \cosh(\eta)} \left\{ C \eta \cosh(\eta) + e^{2\eta \zeta} \right\} \left\{ C \eta \cosh(\eta) + \sinh(\eta) \right\} \\
B = \frac{\varphi_0 e^{-\eta(1+\zeta)}}{(C \eta - 1) \cosh(\eta)} \left\{ C \eta e^{2\eta \zeta} + e^\eta \right\} \left\{ C \eta \cosh(\eta) + \sinh(\eta) \right\}
\]

For $\zeta > \zeta_0$ we can then write

\[
\varphi = \frac{\varphi_0 L}{2\pi D^2} \int_0^\infty d\xi J_0(\xi \ell) \xi \left\{ [C \eta \cosh(\eta[1-\zeta]) + \sinh(\eta[1-\zeta])] [C \eta \cosh(\eta \zeta_0) + \sinh(\eta \zeta_0)] \right\} \\
2C \eta \cosh(\eta) + (1 + C^2 \eta^2) \sinh(\eta)
\]

Comparing the Laplace transform of the photon density with the definition of the electric field correlation function for multiple scattering (1.11)

\[
\bar{\varphi}(p) = \int_0^\infty ds \varphi(s) e^{-ps} \\
g_1(\tau) = \int_0^\infty ds P(s) e^{-\left(\frac{\Delta^2(\tau)}{3s}\right)}
\]

(1.33)
we see a natural parallel between the two forms. $P(s)$ is the probability that a photon will take a path of length $s$. By realizing that $P(s)$ is proportional to the flux of the photon density, we can use Fick’s law

$$P(s) \propto |J_{|z=\xi_0}| = D|\mathbf{n} \cdot \mathbf{\nabla}|$$  \hspace{2cm} (1.34)

to find a direct connection between the electric field auto-correlation function and the Laplace transformed photon density. Given the boundary condition at $\zeta = 1$ and using the non-dimensional notation

$$P(s) \propto CD^* \frac{\partial \varphi}{\partial \zeta} \bigg|_{\zeta = 1} = \frac{cD^* \varphi}{C^*} = \frac{cD^* \left[ 3 L \left( \frac{1 + R}{1 - R} \right) \right]}{2 \pi D^* \left( \frac{1 + R}{1 - R} \right)} \varphi \bigg|_{\zeta = 1} = \frac{c \left( 1 + R \right)}{2 \left( 1 - R \right)} \varphi \bigg|_{\zeta = 1}$$

or simply $P(s) \propto \varphi \big|_{\zeta = 1}$. Letting $\zeta \to 1$ in equation (1.32) yields the expression

$$\overline{P}(s) \propto \varphi \big|_{\zeta = 1}$$

which can be simplified in terms of exponentials as

$$\overline{P}(s) \propto \int_0^\infty d\xi J_0(\xi \ell) \left\{ \frac{C\zeta \left[ C\eta \cosh(\eta \zeta_0) + \sinh(\eta \zeta_0) \right]}{2C\eta \cosh(\eta \zeta_0) + \left( 1 + C^2 \eta^2 \right) \sinh(\eta \zeta_0)} \right\},$$

Rewriting the above integral in terms of the Laplace variable (which is buried in $\alpha$) we exchange $\xi$ for $\alpha$.

$$\eta^2 = \xi^2 + \alpha^2 \quad \Rightarrow \quad \xi = \sqrt{\eta^2 - \alpha^2}, \quad \frac{d\xi}{d\eta} = \frac{\eta}{\sqrt{\eta^2 - \alpha^2}} = \frac{\eta}{\xi}, \quad \eta = \sqrt{\xi^2 + \alpha^2}$$

$$\overline{P}(s) \propto \int_\alpha^\infty d\eta J_0\left( \ell \sqrt{\eta^2 - \alpha^2} \right) C\eta e^{-\eta(1 - \zeta_0)} \frac{(1 + C\eta) - (1 - C\eta) e^{-2\zeta_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}}. \hspace{2cm} (1.35)$$

Knowing that $g_1(t \to 0) = 1$, we normalize $\overline{P}(s)$ to find

$$g_1(\tau) = \frac{\int_\alpha^\infty d\eta J_0\left( \ell \sqrt{\eta^2 - \alpha^2} \right) \eta e^{-\eta(1 - \zeta_0)} \frac{(1 + C\eta) - (1 - C\eta) e^{-2\zeta_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}}}{\int_0^\infty d\eta J_0\left( \ell \sqrt{\eta^2 - \alpha^2} \right) \eta e^{-\eta(1 - \zeta_0)} \frac{(1 + C\eta) - (1 - C\eta) e^{-2\zeta_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}}}. \hspace{2cm} (1.36)$$
When the source is on axis with the detector we have $\ell = 0$, leading to further simplification

$$g_1(\tau) = \frac{\int_{\alpha}^\infty d\eta \eta e^{-\eta(1-\rho_0)} (1 + C\eta) - (1 - C\eta) e^{-2\rho_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}}$$

$$\frac{\int_0^\infty d\eta \eta e^{-\eta(1-\rho_0)} (1 + C\eta) - (1 - C\eta) e^{-2\rho_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}}$$

From the definition of $\alpha$ and comparison of the expressions given in (1.33), we find

$$\alpha(t) = \sqrt{\frac{L}{D^*}} p = \sqrt{\frac{L}{D^*}} \frac{k^2 \langle \Delta r^2(t) \rangle}{3l^*} = \frac{L}{l^*} \sqrt{k^2 \langle \Delta r^2(t) \rangle}.$$  \hspace{1cm} (1.37)

Since equation (1.30) is the Green function for a point source of magnitude $\varphi_0$, we can find how the solution would change if the source were a Gaussian rather than a point by integrating over the distribution.

$$\bar{\varphi} = \frac{\varphi_0 L}{2\pi D^2} \int_{0}^{\infty} d\eta C \eta e^{-\eta(1-\rho_0)} \frac{(1 + C\eta) - (1 - C\eta) e^{-2\rho_0\eta}}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}} \int_{0}^{\infty} dr r^2 \int_{0}^{2\pi} d\theta J_0 \left(r \sqrt{\eta^2 - \alpha^2} \frac{L}{\pi} \right) e^{-4r^2/d^2}$$

Utilizing the fact that $\int_{0}^{\infty} dx e^{-ax} J_0(b\sqrt{x}) = \exp(-b^2/4a)/a$ and thereby substituting $r = \sqrt{x}$ which in turn gives $\int_{0}^{\infty} dr e^{-ar^2} J_0(br)2r = \exp(-b^2/4a)/a$ we can write

$$\bar{\varphi} = \frac{\varphi_0 L}{2\pi D^2} \int_{0}^{\infty} d\eta C \eta e^{-\eta(1-\rho_0)} \frac{(1 + C\eta) - (1 - C\eta) e^{-2\rho_0\eta} \pi d^2}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}} \frac{4}{\pi} e^{-\left(\eta^2 - \alpha^2\right) \left(d^2/4l^*\right)}$$

or in terms of $g_i$

$$g_i(\tau) = \frac{\int_{\alpha}^\infty d\eta \eta e^{-\eta(1-\rho_0)} (1 + C\eta) - (1 - C\eta) e^{-2\rho_0\eta} \pi d^2}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2\eta}} e^{-\left(\eta^2 - \alpha^2\right) \left(d^2/4l^*\right)}$$

\hspace{1cm} (1.38)

where $d$ is the characteristic diameter of the Gaussian. Notice that if $d/L$ is much less than one, then the argument in the exponential becomes very small and therefore the exponential becomes unity.
Appendix 1.D.d  The Solution to the Telegrapher Model in Cylindrical Coordinates

The transport of light in strongly scattering media has been suggested to be accurately described by the so-called two-stream theory.24  Two-stream theory is a 1-dimensional balance of some conservative quantity that must be in motion.  This quantity can therefore only be traveling in one of two directions.  A balance leads to the telegrapher equation in 1-dimension. Durian and Rudnick25 then argue that such an equation can be generalized to 3-dimensions yielding

\[ \frac{\partial}{\partial t} \left( D_\parallel \frac{\partial \varphi}{\partial t} + \varphi \right) = D_\parallel \nabla^2 \varphi. \]  

(1.39)

While the telegrapher equation is somewhat similar to the diffusion equation given by equation (1.23), it does contain an additional second order time derivative. In dimensionless form it is

\[ \frac{\partial}{\partial s} \left( LD_\parallel^* \frac{\partial \varphi}{\partial s} + \varphi \right) = \frac{D_\parallel^*}{L} \nabla^2 \varphi. \]

(1.40)

For the limit of large \( D_\parallel \) equation (1.39) reduces to the wave equation and in the limit of small \( D_\parallel \) the diffusion equation is recovered. Thus, this equation encompasses the regimes for both ballistic and diffusive light transport (see section 1.2.2.3 for comparison with the diffusion equation).

Expanding equation (1.40) in cylindrical coordinates and taking the Laplace transform we have

\[ \frac{\partial^2 \bar{\varphi}}{\partial \ell^2} + \frac{1}{\ell} \frac{\partial \bar{\varphi}}{\partial \ell} + \frac{\partial^2 \bar{\varphi}}{\partial \zeta^2} - \bar{\varphi} \left( p^2 \ell^2 + \frac{L}{D^*} \right) = -\varphi(0) \left( \ell^2 + \frac{L}{D^*} \right). \]

The solution of this equation is written as

\[ \bar{\varphi} = \frac{\beta}{4\pi} \int_0^\infty \frac{\xi}{\eta} J_0(\xi \ell) \left[ \varphi_0 \alpha e^{-\eta K - \zeta K} + A \sinh(\eta \zeta) + B \sinh(\eta [1 - \zeta]) \right] d\xi, \]

where \( \eta^2 \equiv \xi^2 + \alpha^2 \) and

\[ \alpha^2 \equiv \left( p^2 \ell^2 + \frac{L}{D^*} \right) \quad \& \quad \beta \equiv \varphi_0 \left( \ell^2 + \frac{L}{D^*} \right). \]
If we proceed with the steps carried out in section Appendix 1.D.c, the form of the electric field autocorrelation function, \( g_1(\tau) \), is identical to equation (1.38) where only the definition of the parameter \( \alpha \) is different.

\[
\alpha(t) = \left[ \frac{k^2 \langle \Delta r^2(t) \rangle}{3l^*} \right]^2 + \frac{L}{D^*} \frac{k^2 \langle \Delta r^2(t) \rangle}{3l^*} = \frac{L}{l^*} \left[ k^2 \frac{\langle \Delta r^2(t) \rangle}{9} + 1 \right] \tag{1.41}
\]

### Appendix 1.E Calculating Reflectivity

Polarization dependent refractivity coefficient is given by

\[
r_{ij,p} = \frac{n_i \mu_i - n_j \mu_j}{n_i \mu_i + n_j \mu_j} \quad r_{ij,s} = \frac{n_i \mu_i - n_j \mu_i}{n_i \mu_i + n_j \mu_i} \tag{1.42}
\]

where \( \mu_i = \cos(\theta_i) \) and we can use the average of the two polarizations to represent the total reflectivity between a material of indices \( n_i \) and \( n_j \) as \( R_{ij} = (R_{ij,p} + R_{ij,s})/2 \). We can write the reflectivity for three materials (as for the water/glass/air interface) as

\[
R(\mu_1) = \frac{R_{12} + R_{23} - 2R_{12}R_{23}}{1 - R_{12}R_{23}} \tag{1.43}
\]

This expression takes into account the multiple reflections that occur in the middle layer thereby yielding additional reflection of the photons exiting (or trying to exit) the first material. The reflectivity can be averaged over all angles to yield

\[
C_n = \int_0^1 R(\mu) \mu^n d\mu \tag{1.44}
\]

and

\[
R_{avg} = \frac{3C_2 + 2C_1}{3C_2 - 2C_1 + 2} \tag{1.45}
\]

To obtain the coefficients \( C_n \) in equation (1.44), one can integrate using a numerical quadrature method.\cite{22, 26, 27}
Appendix 1.E.a  Consideration of Total Internal Reflectance

One should note for the three-material example given above, the issue of total internal reflectance adds a subtlety into the calculation. In the case where \( n_2 \) is greater than \( n_3 \) (most of the time), there exist angles that are susceptible to total internal reflection. However not all angles from 0° to 90° are present in the second layer. Assessable angles are given from 0° to 90° in the first layer (using Snell’s law). The critical "\( \mu \)" can be found using the following formula

\[
\mu_c = \begin{cases} 
\cos \left[ \arcsin \left( \frac{n_2}{n_1} \right) \right] & (n_2 < n_1) \cap (n_2 < n_3) \\
\cos \left[ \arcsin \left( \frac{n_3}{n_1} \right) \right] & (n_3 < n_1) \cup (n_3 < n_2)
\end{cases}
\]

and thus equation (1.44) is more properly written as

\[
C_n = \int_{0}^{\mu_c} \mu^n d\mu + \int_{\mu_c}^{1} R(\mu) \mu^n d\mu .
\]

Appendix 1.F  Numerical Calculation of \( l^* \)

The transport mean free path is defined in equation (1.10) as

\[
l^* = \frac{l}{1 + \langle \cos \theta \rangle}
\]

where \( l \) is the scattering mean free path and \( \langle \cos(\theta) \rangle \) is the asymmetry parameter. \( l \) is calculated as \( 1/\rho \sigma \) where \( \rho \) is the scatterer number density and \( \sigma \) is the scattering cross-section of each scatterer.\(^3\) Both the scattering cross-section and the asymmetry can be calculated using Mie scattering theory. Mie scattering theory considers the interference effects that occur when a planar electromagnetic wave interacts with a spherical particle of comparable size. The complexity of the solution can be appreciated when one notes the electromagnetic wave can internally reflect multiple times within a particle before emanating as a spherical wave. The relevant equations for calculating \( l^* \) are\(^{28,29}\)
\[
\langle \cos \theta \rangle = \frac{1}{\pi \sigma} \sum_{n=1}^{N} \left[ \frac{n(n+2)}{n+1} \text{Re}(a_n a_{n+1}^* + b_n b_{n+1}^*) + \frac{2n+1}{n(n+1)} \text{Re}(a_n b_n^*) \right],
\]

\[
\sigma = \frac{1}{2\pi} \sum_{n=1}^{N} (2n+1)(|a_n|^2 + |b_n|^2)
\]

where \(x\) is the sphere circumference divided by the wavelength of the incident radiation, and \(a_n\) and \(b_n\) are the Mie scattering coefficients which are an amalgam of spherical Bessel functions operating on the complex refractive index. The sum as written above converges slowly, and instabilities can arise from poor approximations of the spherical Bessel functions. To improve upon the calculation, Lentz suggested calculating the ratio of Bessel functions by using continued fractions in a forward recursion scheme. The improvement yields an efficient and accurate calculation of the spherical Bessel functions to eight digits. The algorithm employed in these studies was written in Matlab, adapted from “Absorption and Scattering of Light by Small Particles”, by Bohren and Huffman. Our calculated \(l^*\) results compared well with those calculated in reference [3].

**Appendix 1.G  Numerical Conversion of \(g_1(\tau)\) to \(\Delta r^2(\tau)\)**

The procedure outlined here requires two basic numerical methods; a root searching algorithm and a quadrature numerical integration technique, both of which can be found in a numerical recipes book. Using equation (1.38)

\[
g_1(\tau) = \frac{\int_{\alpha,\tau}^{\infty} d\eta \eta e^{-\eta(1-\zeta_0)} \left( \frac{(1 + C \eta)}{(1 + C \eta)^2 - (1 - C \eta)^2 e^{-2\eta}} \right) \left( \frac{d}{\pi \eta} \right)^2}{\int_{0}^{\infty} d\eta \eta e^{-\eta(1-\zeta_0)} \left( \frac{(1 + C \eta)}{(1 + C \eta)^2 - (1 - C \eta)^2 e^{-2\eta}} \right) \left( \frac{d}{\pi \eta} \right)^2}
\]

we recognize that the denominator is the normalization and independent of the value for \(\alpha(\tau)\). Analyzing the convergence of the above integral, it is concluded that integrating from \(\eta = 50\) to \(\infty\) contributes negligibly to the total integral for all practical applications. Therefore, for a given data set we can numerically calculate the integral in the denominator \textit{a priori} as

\[
C = \int_{\text{eps}}^{50} d\eta \eta e^{-\eta(1-\zeta_0)} \left( \frac{(1 + C \eta)}{(1 + C \eta)^2 - (1 - C \eta)^2 e^{-2\eta}} \right) \left( \frac{d}{\pi \eta} \right)^2
\]

where \(\text{eps}\) is the computer epsilon. Re-writing equation (1.38)
We must now find the $\alpha(\tau)$ that yields the experimentally determined $g_1^{\text{expt}}(\tau_n)$ using a root searching algorithm, i.e., we find $\alpha(\tau_n) \rightarrow [g_1(\tau_n) - g_1^{\text{expt}}(\tau_n)] = 0$. If we first arrange the list, $\{g_1^{\text{expt}}(\tau_n)\}$, in ascending order, $\{g_1^{\text{expt}}(\tau)\}$ where $g_1^{\text{expt}}(\tau_m) < g_1^{\text{expt}}(\tau_m+1)$, the calculation is expedited by realizing

$$g_1(\tau_{m+1}) = g_1(\tau_m) + \frac{1}{C} \int_{\alpha(\tau_m)}^{\alpha(\tau_{m+1})} d\eta \eta e^{-\eta(1-\alpha)} \frac{(1 + C\eta) - (1 - C\eta)e^{-2C\eta} - (\eta^2 - \alpha^2)(d^2)}{(1 + C\eta)^2 - (1 - C\eta)^2 e^{-2C\eta} e^{-\frac{d^2}{4L}}},$$

which also aids in choosing efficient bounds on the root searching algorithm. Re-ordering $\{g_1^{\text{expt}}(\tau_n)\}$ and the corresponding $\{\alpha(\tau_n)\}$ allows one to calculate the mean square displacement using the diffusion model (equation (1.37)) or the telegrapher model (equation (1.41)). Using a compiled program written in C, the above scheme converts a typical list of several hundred $g_1^{\text{expt}}(\tau_n)$ values in a fraction of a second on a Pentium 4 machine.
References


19. Watanabe, K. (The International Association for the Properties of Water and Steam, Vejle, Denmark, 2003).

20. Fernandez-Prini, R. (The International Association for the Properties of Water and Steam, Erlangen, Germany, 1997).


CHAPTER 2

Probe Particle Dynamics

The dynamical behavior of particles or tracers is dictated by direct and indirect interactions. Direct interactions are electrostatic in origin and are considered instantaneous relative to indirect or hydrodynamic interactions. Direct interactions inherently dictate the stability of the colloidal suspension. In tracer microrheology, stabilized tracer particles are used to probe the causal dynamics leading to bulk material property.

In the following sections the general formalism used to describe probe particle dynamics is presented. Hydrodynamics equations governing single sphere Brownian displacements are developed and compared to experimental data. This data is used as a test case for the bulk of the experimental work presented in the following chapters. In the concluding section, the theoretical interpretation of thermal probe motion in a viscoelastic medium is presented. The fluctuation-dissipation theorem is the underlying framework upon which the rest of the chapters are based.

2.1 A Brief Historical Account of Brownian Motion

In 1785, the Dutch chemist and engineer, Jan Ingnehauz is believed to have made the first recorded observation that charcoal dust placed on an alcohol film performed random displacements.\(^1\) In 1827, similar observations were re-discovered by Robert Brown for whom the phenomenon is now named.\(^1\) Brown originally considered the motion of microscopic particles derived from living material. Through systematic studies of several inanimate materials he concluded that this motion was not necessarily a property of living matter, and speculated that all matter was built of “primitive molecules”.\(^5\)

\(^1\) Inaccurate accounts of the discovery of Brownian motion are found in several texts and continue to be propagated. Specifically, Robert Brown was not the first to observe this phenomenon and the experiments were not done on the erratic motion of pollen particles in water, but rather the material derived from within pollen particles [Shlesinger 2001 & Wilkinson 2005].
The first physical explanation of Brownian motion, as understood today, was given by Delsaux in 1877 as the motion derived from incessant collisions of molecular origin. A critical connection between the diffusive heat flow and random scattering was made by Lord Rayleigh in 1880. In 1888, Leon Gouy performed detailed experiments, eliminating various external perturbations such as vibrations and temperature gradients as the source for the observed movements, thus implying that this motion was an inherent property of the fluid. Gouy also found that a particle’s thermal motion increased with decreasing size and decreasing viscosity of the surrounding fluid.

The French mathematician Louis Bachelier is attributed to have done the first theoretical work on Brownian motion in his Ph.D. thesis entitled *Théorie de la Spéculation* (translated as *The Theory of Speculation*) in 1900. This work is often forgotten in the wake of Albert Einstein’s seminal paper five years later as Einstein and others were apparently unaware Bachelier’s earlier efforts. Despite this, Bachelier’s work is often considered to be more substantial in directly linking stochastic processes such as Brownian motion to a mathematical framework.

In many ways, Einstein brought instant attention to his 1905 and 1906 work on Brownian motion by focusing his arguments on the most controversial issue of the time; the atomic hypothesis which stated that condensed matter was composed of atoms. In this era, there was much speculation that matter could not be reduced to a discrete description; an idea thought to be inconsistent with the laws of thermodynamics, specifically the second law. Einstein’s formulation of the now so-called Einstein equation relating the thermal or Brownian motion of a colloidal particle to the thermal energy is derived from thermodynamic considerations. The thermal energy implicitly incorporates Avagadro’s number which, if determined correctly from experiments, would provide evidence for an underlying discrete nature of matter, *i.e.*, atoms. In 1908, Jean Perrin and a team of students performed impressively precise measurements of the position of colloidal particles as a function of time. The experimental and statistical rigor employed by Perrin and his students eliminated all uncertainty that the Einstein equation was an accurate ensemble description of the particle dynamics.

### 2.2 Einstein’s Description of Brownian Motion

The original Brownian motion description given by Einstein (Appendix 2.A) considered a hypothetical potential field driving a set of particles towards an impenetrable boundary. The induced particle flow sets up a concentration gradient which acts in resistance to the potential field. The strength of this resistance is the diffusivity. At equilibrium, the distribution of particles takes on the form of the Boltzmann distribution, allowing for the determination of the diffusivity as
\[ D_0 = \frac{k_B T}{\zeta} \]  

(2.1)

where \( \zeta \) is the particle friction coefficient.

The apparent simplicity of this derivation often obscures its underlying principles. On one hand, the friction coefficient represents the dissipation of energy via collisions with the surrounding molecules. On the other hand, a Brownian particle will still experience collisions from the surrounding molecules yielding a fluctuating force that causes the particle to undergo superposable random displacements. Thus, the microscopic collisions can be seen as both a random driving force, in analogy with the external field, as well a systematic retardation force. This is an expression of what is now known as linear response theory. That is, the response of a system in thermodynamic equilibrium to an external perturbation is equivalent to that of a spontaneous fluctuation in the absence of this disturbance.\(^{14} \) Observing that both the driving force and retardation force have the same microscopic origin we conclude they must be related. This interrelationship is a statement of the fluctuation-dissipation theorem.

### 2.3 A Microscopic Description of Single Sphere Thermal Fluctuations

On a microscopic length-scale, molecules constantly undergo collisions with each other, randomly transferring energy throughout the system. Thermal motion is the underlying process for the diffusion of mass and energy. For a given property we must take the ensemble average of the system. In the specific case of an ergodic system, a time average of sufficient duration at a single point represents the overall ensemble averaged property. Therefore if we probe the thermal motion of the system at a given point over a sufficient period of time, it is as if we measured the property over the entire ensemble.

Consider a neutrally buoyant sphere of a size-scale much larger than the molecular dimension of the surrounding fluid, yet susceptible to thermal agitation. For now, the surrounding fluid will be considered molecularly small and simple, such as water. The molecularly large sphere is then bombarded by the molecules of the surrounding fluid. At a given time, the sphere will take a step in a random direction dictated by a force imbalance of molecules colliding with one side of the sphere versus the other. Given the disparity in sizes, the displacement of the sphere from any single collision would be difficult, if not impossible, to measure. The time-scale for such collisions for a simple fluid
has been experimentally determined to be on the order of $10^{-14}$ seconds. Each collision does impart some momentum to the sphere and the accumulated effect is experimentally assessable.

Thus far only the collisions as consequence of the solvent molecules fluctuating about have been considered. However the sphere is not a stationary object and once enough momentum is imparted, the sphere experiences a systematic force of the sphere colliding with the solvent. Mathematically, a force balance is written by separating the random and systematic force via the so-called Langevin equation.

$$\frac{dp}{dt} = -\zeta_m \frac{p}{m} + f_B(t)$$  \hspace{1cm} (2.2)

Where $p$ is the momentum, $f_B$ is the random force, and the systematic force is assumed proportional to the velocity, which is presumed valid for small velocities. The proportionality constant is the specific friction coefficient where the subscript $m$ denotes that the quantity is taken as per mass, and is written for an isotropic medium using a scalar value. This coarse grained picture is further developed by expressing the proportionality constant in the systematic force as the hydrodynamic stokes drag on a sphere

$$\frac{dp}{dt} = -\frac{6\pi \eta_0 a}{m_p} p + f_B(t), \hspace{1cm} (2.3)$$

where $\eta_0$ is the viscosity of the solvent and $m_p$ is the mass of the sphere.

### 2.3.1 The Solution to the Langevin Equation

In order to solve the stochastic differential equation given in (2.2), properties of the fluctuating part must be specified. Since $f_B$ arises from a very large number of random collisions, we anticipate at time-scales much larger than the solvent relaxation time the form of $f_B$ is Gaussian with zero mean.

$$\langle f_B(t) \rangle = 0$$ \hspace{1cm} (2.4)

Due to separation in time-scales, we further expect the fluctuating force to be delta correlated

$$\langle f_B(t) f_B(t') \rangle = \frac{G_0 \delta(t - t')}{m_p}$$ \hspace{1cm} (2.5)
where \( G \) is the strength of the fluctuating force. Equation (2.5) is one form of the fluctuation-dissipation theorem.

Integrating equation (2.2) yields

\[
\tilde{p}(t) = \tilde{p}(0) \exp\{-\zeta_m t\} + \int_0^t dt' \tilde{f}_B(t') \exp\{-\zeta_m (t - t')\}.
\]  

(2.6)

It can be shown that the integral on the right-hand side of equation (2.6) is a Gaussian distribution and thus \( p(t) - p(0) \exp\{-\zeta_m t\} \) is also a Gaussian. We find the second moment of this distribution as the mean momentum tensor (see Appendix 2.C)

\[
\{ p(t) \tilde{p}(t) \} = p(0) p(0) e^{-2\zeta t} + G \frac{1}{2\zeta} \left( 1 - e^{-2\zeta t} \right),
\]

which in the long-time limit \( t \gg 1/\zeta_m \) yields,

\[
\{ p(t) p(t) \}_{t \gg 1/\zeta_m} = \frac{G}{2\zeta}. \tag{2.7}
\]

Comparing this expression with the equipartition of energy,

\[
\{ p(t) \tilde{p}(t) \} = m_p k_B T \tilde{I}, \tag{2.8}
\]

we find the strength of the fluctuating force is

\[
G = 2k_B T \zeta \tilde{I}. \tag{2.9}
\]

Further integrating the momentum expression of equation (2.6) leads to the position coordinate

\[
\tilde{r}(t) = \tilde{r}(0) + \frac{p(0)}{\zeta} [1 - \exp\{-\zeta_m t\}] + \frac{1}{\zeta} \int_0^t dt' \tilde{f}_B(t') [1 - \exp\{-\zeta_m (t - t')\}]
\]

(2.10)

where, \( \Delta \tilde{r} \) is a Gaussian random variable. The mean displacement tensor, or second moment of the distribution, is (Appendix 2.C)

\[
\langle \Delta \tilde{r}(t) \Delta \tilde{r}(t) \rangle = p(0) p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta_m t})^2 + 2k_B T \frac{m_p}{\zeta^2} \left[ \zeta_m t - 2 (1 - e^{-\zeta_m t}) + \frac{1}{2} (1 - e^{-2\zeta_m t}) \right]. \tag{2.11}
\]
Recognizing the long-time diffusion coefficient from the Einstein equation (2.1), we can write equation (2.11) in the long-time limit as

\[ \langle \Delta r(t) \Delta r(t) \rangle_{t \gg \zeta_m} = 2D_0 t \hat{I}. \] (2.12)

This expression directly relates the displacement distribution to the long-time diffusion coefficient. The mean square displacement is simply the trace of equation (2.11)

\[ \langle \Delta r^2(t) \rangle = \frac{6D_0}{\zeta_m} \left\{ \zeta_m t - 1 + e^{-\zeta_m t} \right\} \] (2.13)

The mean square displacement is observed to exhibit the proper diffusive ($\Delta r^2(t) \sim t$) and ballistic ($\Delta r^2(t) \sim t^2$) scaling at long and short time-scales, respectively.

### 2.3.2 A Probabilistic Approach: The Smoluchowski Equation

Starting from the ansatz that $\Delta r$ is a random Gaussian variable, we write that the particle probability density function, $\psi(\Delta r, t)$, satisfies the diffusion equation

\[ \frac{\partial \psi}{\partial t} = \nabla \cdot \left( \frac{1}{2} \frac{d \langle \Delta r \Delta r \rangle}{dt} \cdot \nabla \psi \right). \] (2.14)

The above equation is the Smoluchowski equation with no external force. The tensor coefficient is the diffusivity and is related to the velocity autocorrelation function as (see Appendix 2.B)

\[ \frac{1}{2} \frac{d \langle \Delta r \Delta r \rangle}{dt} = \int_0^t \int_0^\infty \langle v(t_0) v(t_0 + \tau) \rangle \, d\tau \] (2.15)

where $\langle v(t_0) v(t_0 + \tau) \rangle$ is the velocity autocorrelation tensor. In the long-time limit the diffusivity tensor attains the value

\[ D_0 = \int_0^\infty \langle v(t_0) v(t_0 + \tau) \rangle \, d\tau, \] (2.16)

which is related to the mean square displacement as follows
\[
\frac{d\langle \Delta r^2(t) \rangle}{dt} \bigg|_{t \to \infty} = \text{Tr} \left\{ \frac{d\langle \Delta r \Delta r \rangle}{dt} \right\} = 2 \text{Tr} \left\{ D_{0} \right\} = 6D_{0},
\]

where, \( \text{Tr}\{\ldots\} \), indicates the trace of the tensor. The above expression shows the connection between the scalar diffusivity and the mean square displacement in the long time limit. Although shown to be valid as \( t \to \infty \), the value for the diffusivity reaches the asymptotic value at a time-scale larger than

\[
\tau^{*} = \int_{0}^{\infty} d\tau \frac{\text{Tr} \{ \langle v(t_{0}) v(t_{0} + \tau) \rangle \}}{\text{Tr} \{ \langle v(t_{0}) v(t_{0}) \rangle \}}.
\]

For \( t \gg \tau^{*} \), equation (2.17) is integrated to find

\[
\langle \Delta r^2(t) \rangle = 6D_{0}t,
\]

which is the same expression found using the Langevin formalism above (equation (2.12)). Recalling the equipartition of energy (equation (2.8)) and definition of the diffusivity tensor (equation (2.16)) the characteristic diffusive time scale is

\[
\tau^{*} = \frac{m_{p}D_{0}}{k_{B}T},
\]

which is the same time scale found in the Langevin formalism (~1/\( \zeta_{m} \)). The Langevin equation is a form of the Smoluchowski equation where the velocity correlations of the particle have relaxed (for \( t \gg \tau^{*} \)). For earlier times the Smoluchowski equation is not valid since the evolution of the probability density function is formulated to be a function of position only. The Fokker-Plank equation is similar in spirit to the Smoluchowski equation, but includes the evolution of the velocity in the probability distribution. As such the Fokker-Plank equation is able to predict the same ballistic limits as the Langevin equation at early times. The time-scale where velocity correlations must be considered is called the Fokker-Plank time-scale, \( \tau_{FP} \).

### 2.4 Inertia and Hydrodynamic Effects

While the success of the Langevin equation is confirmed by its exhibiting the expected ballistic and diffusive behavior at the short- and long-time limits, respectively, the elegantly simple description is not without shortcomings. Specifically, the retardation force is formulated using an instantaneous force law given by what is now known as Stokes drag. However, Stokes’ original result, in 1851, was formulated as a frequency dependent friction coefficient\(^{18,19} \).
where Stokes drag is recovered in the zero frequency limit. In the 1880’s, Basset and Boussinesq independently arrived at a time-dependent expression which includes the effects of the sphere’s motion on the surrounding fluid.\textsuperscript{20, 21} These effects can be incorporated into the Langevin formalism to yield additional terms in the retardation of the sphere motion

\[ \tau_r = \frac{k_BT}{m_s \rho_s} \left( \frac{1}{2} \frac{d^2 \mathbf{p}(t)}{dt^2} - \frac{6 \pi \eta_0 a^2}{m_s} \int_{-\infty}^{t} \frac{1}{\sqrt{t - \tau}} \frac{dp(\tau)}{d\tau} \right). \]  

The last two terms in the extended Langevin equation (ELE) are interpreted as the inertia and self-hydrodynamic effects, respectively. The inertia term contains a solvent equivalent mass, \( m_s \), which is the mass of the solvent that has the same volume as a single particle. The self-hydrodynamic term, sometime referred to as the Basset-Boussinesq force history, accounts for the feedback of sphere motion from earlier times conveyed by the surrounding fluid. As the sphere initially accelerates, the surrounding fluid will circulate from the front to back creating in a vortex ring pattern. The center of this vortex ring grows diffusively until the particle no longer is affected by these self-hydrodynamics. The vorticity effect is observed in the decay of the velocity autocorrelation function from an exponential to a power law. The Basset-Boussinesq force history gives rise to the well-known long-time tail recognized in early simulations of simple fluids.\textsuperscript{18, 22}

Equation (2.21) can be related to the velocity autocorrelation function in the Laplace domain as\textsuperscript{23}

\[ \{ m_p s \} \langle \mathbf{v}(0) \mathbf{v}(s) \rangle + \left[ \frac{1}{2} m_s s + 6 \pi \eta_0 a \left( \frac{a^2 \rho_s}{\eta_0} \right)^{1/2} + 1 \right] \langle \mathbf{v}(0) \mathbf{v}(s) \rangle = k_BT \hat{I} \]  

where \( m_s = 4/3 \pi a^3 \rho_s \). The first term in the curly brackets represents the particle’s inertia and the second curly bracket denotes the fluid force. This equation is represented in the spirit of the fluctuation-dissipation theory where the thermal energy is related to the response of the sphere. Utilizing the initial value property of the Laplace transform, \( \lim_{s \to \infty} \left[ s \mathbf{f}(s) \right] = \lim_{t \to 0} \left[ f(t) \right] \), we find the initial velocity autocorrelation function as

\[ \langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle = \frac{k_BT}{m_p \left( \rho_s + 1 \right)} \text{Tr} \left\{ \hat{I} \right\}. \]  

**References:**

\textsuperscript{20} Basset, A. E. (1883). "On the flow of a body through a perfect fluid with special reference to the motion of a particle and to the flow near the surface of a sphere.

\textsuperscript{21} Boussinesq, J. (1880). "Théorie générale de l'effet de la viscosité dans les équations de l'hydrodynamique.

\textsuperscript{22} Basset, A. E. (1887). "On the motion of a sphere through a rarified fluid.


The above expression is in apparent contradiction with the equipartition of energy. The so-called added mass effect is an artifact of the compressibility assumed in the Langevin equation. A more detailed calculation including compressibility shows that VACF decays from the expected $3k_B T/m_0$ to the value given by equation (2.23) over the time-scale of a sound wave traveling one particle radius.$^{21, 25}$

Using the final value property of the Laplace transform, \[ \lim_{s \to 0} \mathcal{L}^{-1}\{s \tilde{f}(s)\} = \lim_{t \to \infty} \{f(t)\}, \] we find in 3-dimensional space (Appendix 2.D.a)

\[ D_0 = \lim_{t \to \infty} \frac{1}{3} \int_0^t d\tau \langle \psi(0) \cdot \psi(\tau) \rangle. \quad (2.24) \]

Therefore, the expected long-time diffusion coefficient is recovered. The long-time diffusion coefficient scaling is evaluated by expanding equation (2.22) for small values of $s$ yielding

\[ \langle \psi(0) \cdot \psi(t) \rangle = D_0 \frac{3}{2\tau_s \sqrt{\pi}} \left[ \left( \frac{\tau_s}{t} \right)^{3/2} + O\left( \frac{1}{t^2} \right) \right] \]

where $\tau_s \equiv a^2 \rho_s / \eta_0$. Thus, the long-time asymptotic decay of the VACF scales as $t^{-3/2}$ as observed by Alder and Wainwright$^{22}$.

A partial fraction expansion of equation (2.22) allows an analytic expression for the VACF (see Appendix 2.D.b)

\[ \langle \psi(0) \cdot \psi(t) \rangle = g_0 \left[ \frac{\rho_s}{a^2 \eta_0} \left( 3 - \frac{8 \rho_p}{\rho_s} \right) \right]^{1/2} \left\{ \lambda_+ e^{\lambda_+ \xi} \text{Erfc}(\lambda_+ \sqrt{t}) - \lambda_- e^{\lambda_- \xi} \text{Erfc}(\lambda_- \sqrt{t}) \right\} \]

where

\[ \lambda_{\pm} = \pm \frac{3}{2} \sqrt{3 - \frac{8 \rho_p}{\rho_s} \left( 1 + 2 \frac{\rho_p}{\rho_s} \right)}. \]

One will notice for $\rho_p > (5/8) \rho_s$, $\lambda_{\pm}$ is a complex value. Numerical calculations for the complementary error function do not converge for imaginary arguments. However, by considering the exponential term in conjunction with the complementary error function, i.e., $e^{\lambda \xi} \text{Erfc}(z \sqrt{t})$, one forms a special
function also known as the Mittag-Leffler, Villat, or plasma dispersion function, which is convergent for all real and complex values of $z$.

### 2.4.1 Comparison of the Extended and Simplified Langevin Equations

The long-time behavior of the diffusion coefficient found from the simplified Langevin equation (SLE) is obtained in terms of the velocity autocorrelation function as (see Appendix 2.C)

$$D_0 = \lim_{t \to \infty} \frac{1}{3} \int_0^t dt \langle v(0) \cdot v(t) \rangle$$

which is the same expression found in (2.24) for the extended Langevin equation (ELE). Therefore, the area underneath the VACF curve in either formulation is the same and, as will be shown, is a consequence of the fluctuation-dissipation theorem.

---

‡ Technically, the Mittag-Leffler function of half order is defined as $f_{ML}^{\frac{1}{2}}(z) \equiv e^z \text{Erfc}(-iz)$ and the plasma dispersion function is defined as $f_{PD}^{\frac{1}{2}}(z) \equiv e^{-z} \text{Erfc}(-iz)$, however they are simply related by redefining the argument.
Figure 2.1 Comparison of the (---) simplified Langevin equation and the (----) extended Langevin equation for (a) the mean square displacement, (b) the velocity autocorrelation function normalized by the initial velocity, and (c) the time-dependent diffusion coefficient normalized by the long-time diffusion coefficient for a 1 µm polystyrene sphere in water at 20°C.
As shown in Figure 2.1 (b) the SLE predicts the initial velocity correlation to persist over much longer time-scales than the ELE. Thus, the hydrodynamic memory terms drastically alter the time course of the velocity decorrelation as pointed out by several authors.\textsuperscript{18, 26} As a consequence, the time required for the time-dependent diffusion coefficient

$$D(t) \equiv \frac{1}{3} \int_0^t d\tau \langle \mathbf{v}(t_0) \cdot \mathbf{v}(t_0 + \tau) \rangle$$

to reach its asymptotic value is significantly increased (see Figure 2.1 (c)). For the case of a 1 \, \mu \text{m} polystyrene sphere in water, the effects of hydrodynamic memory terms can be seen at times of \sim 10^{-4} seconds. This time-scale is well suited for investigation by diffusing wave spectroscopy.

### 2.5 DWS Measurement of Spheres in Water Over a Range of Temperature and Pressure

Early in the development of DWS, workers took advantage of the accessible small time-scales to verify the scaling of the self-hydrodynamic interaction introduced in subsection 2.4.\textsuperscript{27, 28} Previously, there was sparse experimental evidence to corroborate computer simulations and theoretical predictions.\textsuperscript{29} In this subsection, further experimental evidence is presented over a wide range of conditions. We evaluate the response of thermally driven colloidal spheres in water over a wide range of temperature and pressure. In order to access pressures of 200 MPa, a high pressure scattering cell originally constructed for SANS measurements is used in transmission mode DWS (details can be found in Chapter 1).

In Figure 2.2, the temporal evolution of the mean square displacement is plotted for 420 nm spheres in water at 21\degree C. Using the literature values for the viscosity of water, theoretical curves representing the simplified and extended Langevin equation (equations (2.13) and (2.50), respectively) are generated. From the top plot, it is clear that the experimentally determined mean square displacement is in excellent agreement with the extended Langevin equation. The bottom plot is the mean square displacement divided by time, which further establishes the applicability of the extended Langevin equation description. This representation highlights the time-dependent diffusion coefficient\textsuperscript{§}, allowing observation of the retardation caused by the self-hydrodynamic modes. Given

\textsuperscript{§} \langle \Delta r^2(t)/t \rangle has similar behavior as the time-dependent diffusion coefficient, which is defined as \( D(t) = (1/6) \) \( d(\Delta r^2(t))/dt \). However, \( D(t) \) requires the computation of the numerical derivative, which may significantly enhance small errors in the data.
that the probe is driven by thermal energy alone, such behavior indicates increased velocity correlations rooted in hydrodynamic interactions not accounted for in the simple Langevin equation.

![Figure 2.2](image-url)  

**Figure 2.2** Comparison with theoretically predicted mean square displacement of the simplified (—) and the extended (-----) Langevin equations versus experimental data (○) for 1 wt% 420 nm polystyrene spheres in water at 21°C determined by DWS.
Figure 2.3 The mean square displacement for 32 data sets taken over a temperature range of 20 to 80°C and a pressure range of 0 to 241 MPa for a sample of 1 wt% 421 nm diameter polystyrene spheres in water. Note that all pressures fall on the same line for a given temperature.

Thermal colloidal sphere motion was investigated over a wide range of temperatures and pressures and is plotted in Figure 2.3. The relative lack of response to pressure is expected since the viscosity of water is relatively insensitive to pressure changes. This further establishes that the strength of the thermal fluctuations and colloidal sphere response are dominated by the system temperature.

The influence of temperature on the mean square displacement at ambient pressure is shown in Figure 2.4. The curves represent the best fit of the extended Langevin equation using the viscosity as an adjustable parameter. The extended Langevin equation captures the characteristic shape of the data and predicts viscosities within 10% of literature values. It is apparent that the transition to fully developed diffusive motion appears at longer times with increasing temperature. This owes to the relatively low viscosities of water at high temperatures, which leads to an increase in the
characteristic time-scale for the vorticity diffusion ($\tau_v = a^2 \rho_s / \eta_0$). The inset clearly demonstrates the existence of the $t^{-3/2}$ scaling of the velocity autocorrelation function, the so-called long-time tail.

![Graph](image)

**Figure 2.4** Symbols are the mean square displacement for 420 nm spheres in water from 20 to 80 °C. The lines are fits to the data using the viscosity as an adjustable parameter and the inset is the viscosity autocorrelation function calculated from the fit.

The frequency dependent friction coefficient originally proposed by Stokes and implemented in the extended Langevin equation incorporates memory of the particle’s motion. In this specific case memory of the particle’s motion results from the vorticity induced at early times resulting in an integrodifferential equation with a so-called memory kernel. A natural generalization of this concept is to utilize a frequency dependent friction coefficient as the memory kernel for all linear frequency dependent behavior such as viscoelasticity. This approach yields a generalized Langevin equation consistent with the fluctuation-dissipation theory.
2.6 Fluctuation-Dissipation Formalism

The probabilistic nature of the Smoluchowski equation is similar in spirit to Einstein’s seminal 1905 paper connecting a particle’s diffusivity to the thermal energy of the bath in which it is suspended through the friction coefficient. In subsection 2.3.2 the relationship between a particle’s mobility and its friction coefficient was shown to be (equation (2.16))

\[
\mu = \zeta^{-1} = \frac{1}{3k_B T} \int_0^\infty d\tau \langle \psi(0) \cdot \psi(\tau) \rangle
\]

(2.25)

where we have assumed an isotropic medium such that a single scalar value, \( \mu \), characterizes a particle’s mobility.

The solution of the simplified Langevin equation assumes the fluctuating force is delta correlated owing to a large separation of the solvent and Brownian particle relaxation times. If the time-scales are not sufficiently separated, such as longer lived fluid relaxation, the fluctuation force becomes non-Markovian and some correlation will exist between successive random fluctuations

\[
\langle f_B(t)f_B(t') \rangle = 2k_B T \zeta(t-t') \hat{I}_m.
\]

The correlation strength remains the same as the delta correlated simple Langevin case, following from the limit as \( t \to t' \). A memory kernel formalism is utilized to incorporate particle motion at previous times into the Langevin equation,

\[
\frac{dp(t)}{dt} = -\int_{-\infty}^t dt' \zeta_m(t-t') p(t') + f_B(t).
\]

(2.26)

Equation (2.26) is the so-called generalized Langevin equation (GLE). The simplified Langevin equation is recovered using \( \zeta_m(t-t') \delta(t-t') \) as the memory kernel in the GLE. Taking the Laplace transform of equation (2.26) and using equipartition of energy (see Appendix 2.E) the frequency dependent mobility, or admittance, is found to be

\[
\mu(s) = \frac{1}{m_p s + \zeta(s)} = \frac{1}{3k_B T} \int_0^\infty dt e^{-st} \langle \psi(0) \cdot \psi(t) \rangle.
\]

(2.27)

Equation (2.25) is simply the zero frequency limit of equation (2.27). Equation (2.27) is fundamentally an expression of the fluctuation-dissipation theorem. The generality of this
expression is extended to complex fluids where long-lived relaxation mechanisms give rise to observed elasticity.\textsuperscript{18, 31, 32} Neglecting particle inertial effects, the particle mobility can be recast in terms of viscoelastic functions

$$\frac{1}{\eta(s)} = \frac{2\pi a}{k_B T} \int_0^\infty dt e^{-st} \langle \dot{\mathbf{v}}(0) \cdot \mathbf{v}(t) \rangle.$$ 

Assuming the validity of the Stokes law generalization, the only non-geometric factor left is the frequency dependent viscosity which therefore must contain the details of the fluid dynamical properties. The underlying hypothesis is that stored thermal energy is dissipated through delayed mechanisms accounted for \textit{via} the memory kernel. Thus the fluctuation-dissipation theorem is valid presuming these mechanisms are linear and superposable.

Within the framework of linear viscoelasticity, the memory kernel, $\tilde{\eta}(s)$, is recognized as the complex dynamic viscosity.\textsuperscript{18, 33} Linear viscoelastic functions are easily converted in the Laplace domain allowing for the simple expression of the creep compliance as a function of the VACF in the time domain (Appendix 2.E.a)**.

$J_a(t) = \frac{2\pi a}{k_B T} \int_0^t dt (\tau - t) \langle \dot{\mathbf{v}}(0) \cdot \mathbf{v}(t) \rangle$

In terms of the mean square displacement it follows that (Appendix 2.B)

$$J_a(t) = \frac{\pi a}{k_B T} \langle \Delta v^2(t) \rangle.$$ \hspace{1cm} (2.28)

This is the fundamental equation of microrheology relating the thermal fluctuations of a Brownian probe to the viscoelastic properties of its suspending fluid. Thus, the foundation of microrheology is the fluctuation-dissipation theorem for the special case where the generalized Stokes relationship is valid and the inertia can be neglected.

In the following chapters, experimental investigations of polystyrene latex particle thermal motion in aqueous Pluronic\textsuperscript{TM} solutions are described. Pluronics are poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymers. The tendency of these triblock copolymers to associate and

\textsuperscript{**} The subscript ‘a’ differentiates the “microscopic creep” from that of the bulk creep value. That is to say, the microscopic creep is simply the mean square displacement scaled by the thermal energy. Assuming the validity of the generalized Stokes relationship, the microscopic creep reduces to the suspending medium’s bulk value, \textit{i.e.}, $J_a = J$. 

self-assemble in aqueous solution yields interesting dynamic properties. The thermal response of the polystyrene particles to the viscoelastic nature of the fluid will be described in terms of the microscopic creep. Therefore, concepts developed in traditional rheology will be used to interpret the probe particle dynamics.
Appendix 2.A Einstein’s Classic Derivation

This derivation of the so-called Stokes-Einstein relationship roughly follows that given by Einstein in 1905. Consider an ensemble of Brownian particles where $\int dx \Psi(x)$ is the number of particles and $\Psi(x)$ is the local 1-dimensional number density. For simplicity, Einstein considered an unspecified constant external force, $f_{\text{ext}}$, acting on the particles in one dimension towards an impenetrable boundary. For an arbitrarily small displacement, $\delta x$, the total energy is written as

$$\delta A = \delta U - T\delta S = 0.$$ 

The internal energy is related to the work done by the force, $f_{\text{ext}}$, as

$$\delta U = -\int_0^l dx \Psi(x) f_{\text{ext}} \delta x$$

and entropy is written as

$$\delta S = \int_0^l dx \Psi(x) k_B \frac{\partial \delta x}{\partial x}$$

$$= \int_0^l dx k_B \frac{\partial [\Psi \delta x]}{\partial x} - \int_0^l dx k_B \delta x \frac{\partial \Psi}{\partial x}$$

$$= -\int_0^l dx k_B \delta x \frac{\partial \Psi}{\partial x}$$

yielding

$$0 = -f_{\text{ext}} \Psi + k_B T \frac{\partial \Psi}{\partial x}. \quad (2.29)$$

The force acting on a particle is related to the particle’s velocity through the friction coefficient,

$$f_{\text{ext}} = \zeta v_x.$$ 

This frictional force is balanced by the particle diffusive flux, yielding an expression for the one-dimensional diffusive flux or current

$$j_x = v_x \Psi - D_0 \frac{\partial \Psi}{\partial x}. \quad (2.30)$$
At equilibrium the net current should be zero and upon comparing equations (2.29) and (2.30), the diffusivity is inversely proportional to the friction coefficient

\[ D_0 = \frac{k_B T}{\zeta}. \tag{2.31} \]

Thus, replacing the friction coefficient the expression for the Stokes drag on a sphere of size \( a \) (i.e. \( 6\pi\eta a \)) yields the well-known Stokes-Einstein equation.

Alternatively, specifying that the force, \( f_{ext} \), results from a potential field, \( \phi(x) \), the velocity in equation (2.30) is written as

\[ v_x = -\frac{d\phi(x)/dx}{\zeta}. \]

Given that \( \Psi(x) \propto \exp(-\phi(x)/k_B T) \) (i.e., \( \Psi(x) \) follows the Boltzmann distribution at equilibrium), equation (2.30) is straightforwardly shown to yield the same expression for \( D_0 \) (equation (2.31)).

**Appendix 2.B The Mean Squared Displacement and the Velocity Autocorrelation Function**

There are three commonly cited relations between the velocity autocorrelation function (VACF) and the mean square displacement. First, begin with the definition of a displacement

\[ \Delta r(t) = r(t) - r(0) = \int_0^t dt_1 \Psi(t_1). \tag{2.32} \]

The mean displacement tenor is then

\[ \langle \Delta r(t) \Delta r(t) \rangle = \left\langle \int_0^t dt_1 \Psi(t_1) \int_0^t dt_2 \Psi(t_2) \right\rangle = \int_0^t dt_1 \int_0^t dt_2 \Psi(t_1) \Psi(t_2) \]

In order to simplify the above integral expression for the mean displacement diagram consider the following diagram.
The product of $\langle v(t_1)v(t_2) \rangle$ is symmetric about the diagonal and decays to zero as a function of distance from the diagonal, i.e., as $|t_2 - t_1| \to \infty$, $\langle v(t_1)v(t_2) \rangle \to 0$. The integral can be simplified by only performing the integral over the shaded area.

$$\langle \Delta v(t) \Delta v(t) \rangle = 2 \int_0^t dt_1 \int_0^{t-h} dt' \langle v(t_1)v(t_1 + t') \rangle$$

(2.33)

where $t' \equiv t_2 - t_1$. If the grey lines represent the integration over $t_2$ for a given $t_1$, the first integral from 0 to $t$ is the sum of the grey lines.

The diagram above illustrates this change of variable, such that the horizontal axis in now the deviation from the diagonal, $t'$. The variable change yields a value for $\langle v(t_1)v(t_1 + t') \rangle$ at $t'$ which is the same for all $t_1$. This realization indicates that the VACF is stationary and that $\langle v(t_1)v(t_1 + t') \rangle$ is independent of $t_1$ and can be defined relative to any arbitrarily chosen $t_1 = t_0$, (i.e., $\langle v(t_1)v(t_1 + t') \rangle = \langle v(t_0)v(t_0 + t') \rangle = \langle v(0)v(t') \rangle$). Integrating equation (2.33) by parts yields
\[
\langle \Delta \xi (t) \Delta \xi (t) \rangle = 2 \int_0^t dt_1 \int_0^{t-t_1} dt' \langle \xi(t_0) \xi(t_0 + t') \rangle
\]

\[
dv = dt_1 \rightarrow v = t_1
\]

\[
u(t, t_1) = \int_0^{t-t_1} dt' \langle \xi(t_0) \xi(t_0 + t') \rangle
\]

\[
\frac{du(t, t_1)}{dt_1} = \int_0^{t-t_1} dt' \frac{\partial \langle \xi(t_0) \xi(t_0 + t') \rangle}{\partial t_1} = 0 \quad \text{((\xi(0) \xi(t')) does not vary in } t_1)\]

\[
+ \langle \xi(t_0) \xi(t_0 + t') \rangle \bigg|_{t-t_1} \frac{\partial (t - t_1)}{\partial t_1} - \langle \xi(t_0) \xi(t_0 + t') \rangle \bigg|_{t_0} \frac{\partial (t - t_1)}{\partial t_1}
\]

\[
\frac{du(t, t_1)}{dt_1} = -\langle \xi(t_0) \xi(t_0 + t - t_1) \rangle
\]

leading to a single integration description of the mean displacement

\[
\langle \Delta \xi (t) \Delta \xi (t) \rangle = 2 \int_0^t dt_1 \int_0^{t-t_1} dt' \langle \xi(t_0) \xi(t_0 + t') \rangle
\]

\[
= 2h \int_0^{t-t_1} dt' \langle \xi(t_0) \xi(t_0 + t') \rangle \bigg|_{t-t_1}^{t} - 2 \int_0^{t} dt_1 t_1 (-1) \langle \xi(t_0) \xi(t_0 + t - t_1) \rangle.
\]

\[
= 2 \int_0^t dt_1 t_1 \langle \xi(t_0) \xi(t_0 + t - t_1) \rangle
\]

Further defining \( \tau \equiv t - t_1 \) yields one of the most common expressions connecting the mean square displacement to the velocity autocorrelation function

\[
\langle \Delta \xi (t) \Delta \xi (t) \rangle = 2 \int_{\tau=t}^{\tau=t-t} (-1) d\tau (t - \tau) \langle \xi(t_0) \xi(t_0 + \tau) \rangle
\]

\[
= 2 \int_0^t d\tau (t - \tau) \langle \xi(t_0) \xi(t_0 + \tau) \rangle
\]

Differentiating equation (2.34) and recalling Leibnitz’s rule establishes the connection between the time derivative of the mean square displacement and the velocity autocorrelation function

\[
\frac{d}{dt} \langle \Delta \xi (t) \Delta \xi (t) \rangle = 2 \frac{d}{dt} \int_0^t dt' \langle \xi(t_0) \xi(t_0 + t') \rangle
\]

\[
= 2 \int_0^t dt' \frac{\partial}{\partial t} \langle \xi(t_0) \xi(t_0 + t') \rangle
\]

\[
+ 2 (t - t') \langle \xi(t_0) \xi(t_0 + t') \rangle \bigg|_{t-t} \frac{\partial}{\partial t} - 2 (t - t') \langle \xi(t_0) \xi(t_0 + t') \rangle \bigg|_{t_0} \frac{\partial}{\partial t} \]

\[
= 2 \int_0^t dt \langle \xi(t_0) \xi(t_0 + t) \rangle
\]
Thus we find a second common expression relating the mean square displacement to the velocity autocorrelation function. This relation is often written as

\[
\frac{1}{2} \frac{d}{dt} \langle \Delta r(t) \Delta r(t) \rangle = \int_0^t d\tau \langle \dot{\mathbf{v}}(t_0) \cdot \mathbf{v}(t_0 + \tau) \rangle
\]

(2.35)

where the left hand side is oftentimes identified as the diffusivity tensor. This expression in turn defines the so-called time-dependent diffusion constant, \(\text{Tr} \{ D \} = 3 D(t) = \int_0^t d\tau \langle \dot{\mathbf{v}}(t_0) \cdot \mathbf{v}(t_0 + \tau) \rangle\).

Differentiating with respect to time a second time establishes the connection between the mean displacement and the most general tensor form of the velocity autocorrelation function

\[
\frac{1}{2} \frac{d^2}{dt^2} \langle \Delta r(t) \Delta r(t) \rangle = \frac{d}{dt} \int_0^t d\tau \langle \dot{\mathbf{v}}(t_0) \cdot \mathbf{v}(t_0 + \tau) \rangle
\]

\[
= \int_0^t d\tau \frac{\partial}{\partial t} \langle \dot{\mathbf{v}}(t_0) \mathbf{v}(t_0 + \tau) \rangle_{t=0}^{\tau=0}
\]

\[
+ \langle \dot{\mathbf{v}}(t_0) \mathbf{v}(t_0 + \tau) \rangle_{t=0}^{\tau=0} \frac{\partial}{\partial t} \langle \mathbf{v}(t_0 + \tau) \rangle_{t=0}^{\tau=0}
\]

\[
= \langle \mathbf{v}(t_0) \mathbf{v}(t_0 + t) \rangle.
\]

(2.36)

For the case of an isotropic medium, the trace of the tensor (or dot product) characterizes the VACF without loss of information

\[
\langle \mathbf{v}(t_0) \mathbf{v}(t_0 + t) \rangle = \text{Tr} \{ \langle \mathbf{v}(t_0) \mathbf{v}(t_0 + t) \rangle \} = \frac{1}{2} \text{Tr} \left( \frac{d^2}{dt^2} \langle \Delta r(t) \Delta r(t) \rangle \right) = \frac{1}{2} \frac{d^2}{dt^2} \langle \Delta r^2(t) \rangle \]

(2.37)

**Appendix 2.C  The Mean Momentum and Position Coordinate from the Langevin Equation**

The Gaussian nature of the momentum is demonstrated reconsidering equation (2.6)

\[
p(t) - p(0) \exp \{ -\zeta_m t \} = \int_0^t dt' \int_B(t') \exp \{ -\zeta_m (t - t') \}.
\]

(2.6)
Separating the total time integration into $N$ individual integrals such that each corresponds to a time step $\Delta t$ (i.e., $N \Delta t = t$) yields

$$p(t) - p(0) \exp \{-\zeta_m t\} = \sum_{n=0}^{N-1} \int_{n\Delta t}^{(n+1)\Delta t} dt' f_B(t') \exp \{-\zeta_m (t - t')\}$$

(2.38)

Choosing sufficiently small time steps such that $\Delta t \ll 1/\zeta$, yet large enough that $f_B$ exhibits several delta correlated realizations (i.e., $\gg 10^{14}$), the exponential part is effectively constant

$$p(t) - p(0) \exp \{-\zeta_m t\} = \sum_{n=0}^{N-1} \exp \{-\zeta_m (t - n\Delta t)\} \int_{n\Delta t}^{(n+1)\Delta t} dt' f_B(t').$$

(2.39)

Since each of the integrals in the sum are Gaussians of zero mean, their sum must also be Gaussian and therefore so must the left hand side of the equation. The mean momentum tenor is the second moment of this distribution (i.e., from equation (2.6))

$$\langle p(t) p(t) \rangle = p(0)^2 e^{-2\zeta_m t} + 2p(0) e^{-\zeta_m t} \int_0^t dt_1 \langle f_B(t_1) \rangle e^{-\zeta_m (t-t_1)}$$

$$+ \int_0^t dt_1 \int_0^t dt_2 \langle f_B(t_1) f_B(t_2) \rangle e^{-\zeta_m (t-t_1)} e^{-\zeta_m (t-t_2)}.$$

Recalling the properties of $\langle f_B \rangle$ given previously in equations (2.4) and (2.5) allows for simplification to the second and third terms on the right hand side

$$\langle p(t) p(t) \rangle = p(0)^2 e^{-2\zeta_m t} + \int_0^t dt_1 \int_0^t dt_2 G \delta(t_1 - t_2) e^{-\zeta_m (t-t_1)} e^{-\zeta_m (t-t_2)}$$

$$= p(0)^2 e^{-2\zeta_m t} + \int_0^t dt e^{2\zeta_m t}$$

$$= p(0)^2 e^{-2\zeta_m t} + G \frac{1}{2\zeta_m} (1 - e^{-2\zeta_m t}).$$

If $t \gg 1/2\zeta_m$, equation (2.7) is recovered

$$\langle p(t) p(t) \rangle = \frac{G}{2\zeta_m}.$$

The position coordinate is obtained by integrating the momentum in equation (2.6)

$$r(t) = r(0) + \frac{p(0)}{\zeta} [1 - \exp \{-\zeta_m t\}] + \frac{1}{\zeta} \int_0^t dt' f_B(t') [1 - \exp \{-\zeta_m (t - t')\}].$$

(2.40)
In analogy with the previous discussion of the Gaussian nature of the momentum similar arguments demonstrate that the displacement variable, $\Delta r_i$, is also Gaussian. The mean displacement tensor is the second moment of the $\Delta r$ distribution

$$
\langle \Delta r(t) \Delta r(t') \rangle = p(0) p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta t})^2 + p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta t}) \int_0^t dt_1 \langle f_B(t_1) \rangle (1 - e^{-\zeta(1-t_1)})
$$

$$
+ \frac{1}{\zeta^2} \int_0^t dt_1 \int_0^{t'} dt_2 \langle f_B(t_2) \rangle (1 - e^{-\zeta(1-t_2)}) (1 - e^{-\zeta(1-2t_2)})
$$

Once again recalling the properties of $\langle f_B \rangle$ given in equations (2.4) and (2.5) the mean displacement tensor is

$$
\langle \Delta r(t) \Delta r(t') \rangle = p(0) p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta t})^2
$$

$$
+ \frac{1}{\zeta^2} \int_0^t dt_1 \int_0^{t'} dt_2 \langle f_B(t_1) \rangle (1 - e^{-\zeta(1-t_1)}) (1 - e^{-\zeta(1-2t_2)})
$$

$$
= p(0) p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta t})^2 + G \frac{1}{\zeta^2} \int_0^t dt_1 \left[ 1 - 2e^{-\zeta(1-t_1)} - e^{-\zeta(2t_1)} \right]
$$

$$
= p(0) p(0) \frac{1}{\zeta^2} (1 - e^{-\zeta t})^2 + \frac{G m_p}{\zeta^4} \left[ \zeta_m t - 2(1 - e^{-\zeta t}) + \frac{1}{2} (1 - e^{-2\zeta t}) \right]
$$

For short times ($t \ll 1/\zeta_m$) the mean square displacement scales ballistically (i.e., $\langle \Delta^2 r(t) \rangle \sim t$),

$$
\langle \Delta r(t) \Delta r(t) \rangle |_{t < 1/\zeta_m} = p(0) p(0) \frac{t^2}{m_p}.
$$

(2.42)

Recalling the fluctuation strength ($G = 2k_B T \zeta$, i.e., equation (2.9)) at sufficiently long times ($t \gg 1/\zeta_m$) the mean displacement tensor becomes

$$
\langle \Delta r(t) \Delta r(t) \rangle |_{t > 1/\zeta_m} = G \frac{1}{\zeta^2} t = 2\frac{k_B T}{\zeta} t \frac{1}{t \zeta}.
$$

(2.43)

Therefore, in the long-time limit the mean square displacement scales diffusively (i.e., $\langle \Delta^2 r(t) \rangle \sim t$).

An alternative route to the above result is to solve the Langevin equation by letting the term $dp/\zeta m_p dt \to 0$, thereby neglecting the inertia.

The mean square displacement is the trace of equation (2.41)

$$
\langle \Delta r^2(t) \rangle = \text{Tr} \left[ p(0) p(0) \right] \frac{1}{\zeta^2} (1 - e^{-\zeta t})^2 + \text{Tr} \left[ G \right] \frac{m_p}{\zeta^3} \left[ \zeta_m t - 2(1 - e^{-\zeta t}) + \frac{1}{2} (1 - e^{-2\zeta t}) \right].
$$
The right hand side can be further developed utilizing the equipartition of energy (equation (2.8)) and knowledge of the fluctuation strength (equation (2.9)) yielding

\[
\langle \Delta r^2(t) \rangle = 3k_B T \frac{m_p}{\zeta^2} (1 - e^{-\zeta_m t})^2 + 6k_B T \frac{m_p}{\zeta^2} \left[ \zeta_m t - 2(1 - e^{-\zeta_m t}) + \frac{1}{2}(1 - e^{-2\zeta_m t}) \right]
\]

\[
= 6D_0 \frac{1}{\zeta_m} \left( \frac{1}{2}(1 - e^{-\zeta_m t})^2 + \zeta_m t - 2(1 - e^{-\zeta_m t}) + \frac{1}{2}(1 - e^{-2\zeta_m t}) \right)
\]

\[
= 6D_0 \frac{1}{\zeta_m} \left[ \zeta_m t - 1 + e^{-\zeta_m t} \right]
\]

Defining the time-dependent diffusion coefficient \( D(t) \equiv (1/6) d\langle \Delta r^2(t) \rangle / dt \), yields

\[
D(t) = \frac{1}{2} \frac{d}{dt} \langle \Delta r^2(t) \rangle = D_0 \left( 1 - e^{-\zeta_m t} \right).
\]

Recalling equation (2.36) the velocity autocorrelation function is simply

\[
\langle v(0) \cdot v(t) \rangle = \frac{1}{2} \frac{d^2 \langle \Delta r^2(t) \rangle}{dt^2} = 3D_0 \zeta_m e^{-\zeta_m t}.
\]

Integrating the velocity autocorrelation function with respect to time in the long time limit yields

\[
\lim_{t \to \infty} \int_0^t dt \langle v(0) \cdot v(t) \rangle = \int_0^\infty dt \, 3D_0 \zeta_m e^{-\zeta_m t}
\]

\[
= 3D_0 \zeta_m \left[ \frac{e^{-\zeta_m t}}{-\zeta_m} \right]_0^\infty
\]

which in turn leads to the expected expression for the long time diffusion coefficient

\[
D_0 = \lim_{t \to \infty} \frac{1}{3} \int_0^t dt \langle v(0) \cdot v(t) \rangle. \quad (2.44)
\]
Appendix 2.D  The Extended Langevin Equation

Laplace transformation of the Langevin equation including the Basset-Boussinesq force history terms yields\(^{23}\)

\[
\left\{ \frac{4}{3} \pi a^3 \rho_p s \right\} \langle \dot{\mathbf{x}}(0) \mathbf{\bar{u}}(s) \rangle + \left[ \frac{2}{3} \pi a^3 \rho_s s + 6 \pi \eta_0 a \left( \frac{a^2 s \rho_s}{\eta_0} \right)^{1/2} + 1 \right] \langle \mathbf{v}(0) \mathbf{\bar{u}}(s) \rangle = k_B T \dot{I} \tag{2.45}
\]

where the first term in the curly brackets represents the particle inertia and the second term accounts for the fluid force. This expression is presented in the spirit of the fluctuation-dissipation theorem where the thermal energy is related to the response of the sphere. The velocity autocorrelation tensor in the Laplace domain is isolated as

\[
\langle \mathbf{v}(0) \mathbf{\bar{u}}(s) \rangle = \frac{k_B T}{6 \pi \eta_0 a} \dot{I} - \frac{\left[ \frac{2}{3} \pi a^3 \rho_s s + 6 \pi \eta_0 a \left( \frac{a^2 s \rho_s}{\eta_0} \right)^{1/2} + 1 \right]}{1 + \left( \frac{a^2 s \rho_s}{\eta_0} \right)^{1/2} + \frac{8 a^2 \rho_s}{9 \eta_0} \left( 1 + \frac{2 \rho_p}{\rho_s} \right)} \tag{2.46}
\]

where

\[
\dot{I} = \frac{k_B T}{6 \pi \eta_0 a} \dot{I} \quad \tau_v = \frac{a^2 \rho_s}{\eta_0} \quad \beta = \frac{\tau_v}{9} \left( 1 + \frac{2 \rho_p}{\rho_s} \right)
\]

leading to the following description of the velocity autocorrelation function in the Laplace domain

\[
\langle \mathbf{v}(0) \mathbf{\bar{u}}(s) \rangle = \frac{D}{1 + (\tau_v s)^{1/2} + \beta s} \tag{2.47}
\]

Appendix 2.D.a  Limiting Behavior

The Laplace domain provides convenient access to the short- and long-time limits. Employing the initial value property of the Laplace transform, \( \lim_{s \to \infty} [s \mathbf{\bar{u}}(s)] = \lim_{t \to 0} [f(t)] \), the short-time behavior of the velocity autocorrelation function is captured
\[
\lim_{s \to \infty} [s \langle \nabla(0) \nabla(s) \rangle] = \frac{D}{\beta} = \frac{k_B T}{6 \pi \mu a} \left( 1 + \frac{\rho_p}{\rho_s} \right) \left( \frac{2}{3} \pi \rho_s^3 \rho_p \right) = \frac{k_B T}{m_p \left( \frac{\rho_s}{2 \rho_p} + 1 \right)}
\]

\[
\langle v(0) \cdot v(0) \rangle = \frac{k_B T}{m_p \left( \frac{\rho_s}{2 \rho_p} + 1 \right)} \text{Tr} \{ \hat{I} \}
\]

where the last expression is the equipartition of energy accounting for the so-called added mass effect due to the acceleration of the particle. This effect is owed to the assumed incompressibility of the solvent and is a result of momentum being additionally partitioned to the solvent via the production of sound waves.\(^{25, 34}\)

Recalling the following property of the Laplace transform

\[
\frac{\langle v(0) \cdot \nabla(s) \rangle}{s} = \int_0^\infty dt e^{-st} \int_0^t d\tau \langle v(0) \cdot \nabla(\tau) \rangle,
\]

and utilizing the final value property of the Laplace transform, \( \lim_{s \to 0} [s \hat{f}(s)] = \lim_{t \to \infty} [f(t)] \), yields

\[
\lim_{s \to 0} \left[ s \frac{\langle v(0) \cdot \nabla(s) \rangle}{s} \right] = D_0 \text{Tr} \{ \hat{I} \}.
\]

The expected long-time diffusion coefficient is easily recovered\(^{35}\)

\[
D_0 = \lim_{t \to \infty} \frac{1}{3} \int_0^t d\tau \langle v(0) \cdot \nabla(\tau) \rangle.
\]

The particle and fluid inertia significantly affect the long-time scaling of the particle’s velocity autocorrelation function. This can be seen by considering the small \( s \) limit of equation (2.46) and transforming to the time domain\(^{23}\)

\[
\langle v(0) \psi(t) \rangle = \frac{D}{2\tau_v \sqrt{\pi}} \left[ \left( \frac{\tau_v}{t} \right)^{3/2} + O \left( \frac{1}{t^2} \right) \right]
\]
which clearly demonstrates the algebraic decay of the velocity correlations, or the well-known long-time tail.26

Appendix 2.D.b Solution to the Extended Langevin Equation

A partial fraction expansion of equation (2.47) yields

\[
\left\langle \mathbf{v}(0) \mathbf{v}(s) \right\rangle = \frac{D}{1 + (\tau v)^2 + \beta s} = \frac{D}{\sqrt{\tau \beta}} \left\{ \frac{\sqrt{\tau \beta}}{\sqrt{\tau \beta} + \sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}} \right\}
\]

\[
= \frac{D}{\sqrt{\tau \beta} - \sqrt{y^2}} \left\{ \frac{\sqrt{\tau \beta} (\sqrt{\tau \beta} + \sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}})}{\sqrt{\tau \beta} + \sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}} \right\}
\]

\[
= \frac{D}{1 + \left(\frac{\sqrt{\tau \beta} + \sqrt{y^2}}{\sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}} \right) + \frac{1}{\sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}}}
\]

where \(x\) and \(y\) are

\[
\sqrt{\tau \beta} = \frac{\sqrt{x^2 + \sqrt{y^2}}}{\sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}} \quad \text{and} \quad \beta = \frac{1}{\sqrt{x^2 + \sqrt{\tau \beta}}}.
\]

(2.48)

Recalling the identity26

\[
\mathcal{L} \left\{ e^{\tau t} \text{Erfc}\sqrt{x t} \right\} = \frac{1}{\sqrt{\tau \beta} + \sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}},
\]

the velocity autocorrelation tensor is written as

\[
\left\langle \mathbf{v}(0) \mathbf{v}(t) \right\rangle = \mathcal{L}^{-1} \left\{ \left\langle \mathbf{v}(0) \mathbf{v}(s) \right\rangle \right\} = D \frac{\sqrt{\tau \beta}}{\sqrt{\tau \beta} - \sqrt{y^2}} \left\{ \sqrt{\tau \beta} e^{\tau t} \text{Erfc}\sqrt{x t} - \sqrt{y^2} e^{\tau t} \text{Erfc}\sqrt{y^2} \right\}.
\]

Finally solving for \(\sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}}\) in expression (2.48)

\[
\beta x - \sqrt{\tau \beta} \sqrt{x^2 + \sqrt{\tau \beta} + \sqrt{y^2}} + 1 = 0 \quad \beta y - \sqrt{\tau \beta} \sqrt{y^2} + 1 = 0
\]

and
The analytic expression for the velocity autocorrelation tensor is

\[
\langle \mathbf{v}(0) \mathbf{v}(t) \rangle = \mathcal{L}^{-1} \{ \langle \mathbf{v}(0) \mathbf{v}(s) \rangle \} = D \lambda_+ \lambda_- \left\{ \lambda_+ e^{\lambda_+ t} \text{Erfc}(\sqrt{\tau_v} \lambda_+) - \lambda_- e^{\lambda_- t} \text{Erfc}(\sqrt{\tau_v} \lambda_-) \right\}
\]

with the velocity autocorrelation function defined as the trace of the tensor (or dot product)

\[
\langle \mathbf{v}(0) \cdot \mathbf{v}(t) \rangle = 9 D_0 \tau_v \left[ \frac{5 - 8 \frac{\rho_p}{\rho_s}}{} \right]^{1/2} \left\{ \lambda_+ e^{\lambda_+ t} \text{Erfc}(\sqrt{\tau_v} \lambda_+) - \lambda_- e^{\lambda_- t} \text{Erfc}(\sqrt{\tau_v} \lambda_-) \right\}
\]

where \( \text{Erfc}(\cdot) \) is the complex complement of the error function. In the limit that \( \rho_p/\rho_s \rightarrow \infty \) equation (2.49) reduces to the typical Langevin result where the velocity autocorrelation function decays exponentially. The mean square displacement is found from equation (2.34) in the Laplace domain, i.e., \( \langle \Delta \tilde{r}^2(s) \rangle s^2 = 2 \langle \tilde{v}(s) \cdot \tilde{v}(0) \rangle \). Following a fairly tedious partial fraction expansion

\[
\langle \Delta \tilde{r}^2(s) \rangle = \frac{6 D_0}{s^2 \left[ 1 + (\tau_v s)^{1/2} + \beta s \right]}\left[ 1 \right]
\]

which upon inversion yields
Similarly, the following expression for the time-dependent diffusion coefficient is obtained

\[
\tilde{D}(s) = \frac{\langle v(0) \tilde{v}(s) \rangle}{3s} \text{ (see equation (2.35))}
\]

or in the time domain

\[
D(t) = D_0 \left[ 1 + 3 \left( 5 - \frac{8}{\rho_s} \right) \right]^{-1/2} \left[ \frac{e^{\xi t} \text{Erfc}(\lambda_+ \sqrt{t}) - e^{\xi t} \text{Erfc}(\lambda_- \sqrt{t})}{\lambda_+} \right].
\]  

(2.51)

**Appendix 2.D.c The Calculation of the Complex Complementary Error Function**

The complementary error function is defined as

\[
\text{Erfc}(\zeta) \equiv \frac{2}{\sqrt{\pi}} \int_{\zeta}^{\infty} dt e^{-t^2}
\]

where for the purposes of this calculation, \( \zeta \) is a complex value. As mentioned above, numerical calculations of the complementary error function do not converge for imaginary arguments. Thus, one must consider the product of an exponential and the complementary error function, where

\[
w(z) = e^{-z^2} \text{Erfc}(-iz)
\]

is also known as the plasma dispersion function. The plasma dispersion function is directly related to the Mittag-Leffler function of \( \frac{1}{2} \) order. This function is generally used in fractional calculus, which is of particular relevance since the Basset-Boussinesq force history term in equation (2.21) can be expressed as a fractional derivative\(^3\), \( e.g., \).
\[
\frac{1}{\sqrt{\pi}} \int_0^t dt' \frac{1}{\sqrt{t-t'}} \frac{dV(\tau)}{d\tau} = \frac{d^{1/2}}{dt^{1/2}} V(\tau).
\]

In our case, equation (2.49), the term \(e^{z^2} \text{Erfc}(z\sqrt{t})\) is related to the plasma dispersion function \(w(iz\sqrt{t})\). The numerical algorithm utilized in these studies follows that of Poppe and Wijers\(^3\) which is based on the work of Gautschi\(^3\). Numerical calculations were compared to references 40 and 41.

**Appendix 2.E The Generalized Langevin Equation and Linear Viscoelastic Functions**

The Generalized Langevin equation is expressed as the following integrodifferential equation (i.e., equation (2.26) above)

\[
\frac{dp(t)}{dt} = -\int_{-\infty}^{t} dt' \zeta_m(t-t') p(t') + F_B(t),
\]

which following Laplace transformation becomes

\[
\tilde{p}(s) s - p(0) = -\tilde{\zeta}_m(s) \tilde{p}(s) + \tilde{F}_B(s).
\]

The ensemble average of the product of the momentum and initial momentum is

\[
\langle p(0) \tilde{p}(s) \rangle s - \langle p(0) p(0) \rangle = -\tilde{\zeta}_m(s) \langle p(0) \tilde{p}(s) \rangle + \langle p(0) \tilde{F}_B(s) \rangle = 0
\]

where the lack of correlation between the Brownian force and the initial velocity has been incorporated. Dividing through by \(m_p\) and rearranging the above equation in the spirit of linear response theory yields the transfer function of the generalized Langevin equation

\[
\frac{1}{s + \tilde{\zeta}_m(s)} = \frac{\langle p(0) \tilde{p}(s) \rangle}{\langle p(0) p(0) \rangle}.
\]

Taking the dot product of the velocity autocorrelation function and utilizing the equipartition of energy (equation (2.8)) yields
This is the generalized expression of the fluctuation-dissipation theorem introduced previously in equation (2.27). Neglecting inertial effects ($m_p s$) and assuming that the generalized Stokes relationship is valid, $\zeta(s) = 6\pi a\eta(s)$, establishes the following relationship for the frequency dependent viscosity in the Laplace domain

$$\frac{1}{\eta(s)} = \frac{2\pi a}{k_BT} \int_0^\infty dt e^{-st} \left\langle \dot{\gamma}(0) \cdot \ddot{\gamma}(t) \right\rangle.$$  

Of course, the frequency dependent viscosity is also readily related to the mean square displacement in the Laplace domain using equation (2.34)

$$\frac{1}{\eta(s)} = \frac{2\pi a}{k_BT} \left\langle \dot{\gamma}(0) \cdot \ddot{\gamma}(s) \right\rangle = \frac{\pi a}{k_BT} s^2 \left\langle \Delta \vec{r}^2(s) \right\rangle$$  \hspace{1cm} (2.52)

**Appendix 2.E.a Linear Viscoelastic Functions**

Linear viscoelastic functions essentially are memory kernels that map the rate of strain to the stress or the rate of stress to the strain as

$$\sigma(t) = \int_{-\infty}^t d\tau G(t - \tau) \frac{d\gamma}{d\tau}(\tau) \quad \text{and} \quad \gamma(t) = \int_{-\infty}^t d\tau J(t - \tau) \frac{d\sigma}{d\tau}(\tau)$$

where $G(t)$ and $J(t)$ are the stress relaxation modulus and creep compliance, respectively.\(^{33, 42}\) Laplace transforming the above expressions

$$\tilde{\sigma}(s) = s\tilde{G}(s) \tilde{\gamma}(s) \quad \text{and} \quad \tilde{\gamma}(s) = s\tilde{J}(s) \tilde{\sigma}(s)$$

and subsequently rearranging them leads to the following relation

$$s\tilde{G}(s) = \frac{1}{s\tilde{J}(s)}.$$  \hspace{1cm} (2.53)
Oftentimes, the Laplace transformed stress relaxation modulus is called the complex viscosity \((i.e., \quad G_s(s) = \tilde{\eta}(s))\). While this term tends to be reserved for the frequency domain, the quantities can be equated through analytic continuation. Thus, combining equations (2.53) and (2.52) yields

\[
\tilde{J}_a(s) = \frac{1}{s^2\tilde{\eta}(s)} = \frac{\pi a}{k_B T}\langle \Delta r^2(s) \rangle,
\]

which in turn is easily inverted to the time domain

\[
J_a(t) = \frac{\pi a}{k_B T}\langle \Delta r^2(t) \rangle
\]

thereby directly relating the suspending medium’s creep compliance to the particle mean square displacement.\(^\dagger\dagger\)

In the frequency domain the complex stress relaxation modulus (or complex modulus) is defined as

\[
G^* \equiv i\omega G_r(i\omega) = G'(\omega) + iG''(\omega),
\]

which consists of both real and imaginary part.\(^\ddagger\ddagger\) The real part, \(G'(\omega)\), is the elastic or storage modulus and the imaginary part, \(G''(\omega)\), is the viscous or loss modulus. Thus, the complex modulus can be viewed as the elastic susceptibility of the material in analogy with dielectric susceptibility in electromagnetism or admittance in linear circuit analysis. In the linear regime, the complex modulus is entirely determined by the frequency.

A similar expression can be written for the complex creep compliance (or complex compliance)

\[
J^* \equiv i\omega J_r(i\omega) = J'(\omega) - iJ''(\omega)
\]

where \(J'(\omega)\) and \(J''(\omega)\) are the storage and loss compliances, respectively. Reference to equation (2.53) indicates that

\(^\dagger\dagger\) The subscript ‘\(a\)’ denotes the microscopic creep compliance, which is equal to the bulk creep compliance provided that the probe does not significantly affect the suspending medium and that the generalized Stokes relationship is valid.

\(^\ddagger\ddagger\) The traditional field of rheology will typically use \(G(t)\) as the stress relaxation modulus, however the so-called microrheology community tends use the notation of \(G_r(t)\) (note the subscript “\(r\)”). To confuse the enemy, microrheology literature often defines \(G(s)\) (without the subscript) as the complex modulus in the Laplace domain \((i.e., \quad G(s) = sG_r(s) = s\tilde{\eta}(s))\). For reference on proper rheological nomenclature see Ferry 1980 or Dealy 1995.
\[ G' (\omega) = \frac{J' (\omega)}{J'^2 (\omega) + J''^2 (\omega)} \quad \text{and} \quad G'' (\omega) = \frac{J'' (\omega)}{J'^2 (\omega) + J''^2 (\omega)}. \] (2.54)

**Appendix 2.E.b Transformation of Linear Viscoelastic Functions**

One major difficulty in determining the storage and loss modulus from microrheology data is transforming from the time domain to the Laplace (or frequency) domain. Direct Fourier transformation typically yields poor results due to truncation errors most evident at the time extremes. Another approach is to approximate the mean square displacement as a local power law which ultimately requires the numerical calculation of the derivative.\(^{43}\) A further extension of this method uses the second derivative in order to better capture large changes in slope.\(^{44}\) However, it is well-known that numerical calculation of the derivative may significantly enhance small errors in the data. Thus, large smoothing of the data is required, which reduces the problem of Laplace transformation to carrying out a second order spline fit of the data.

An alternative method proven to yield better results utilizes a rheological model to fit the data. The simplest is the Maxwell model which contains a single storage and relaxation mechanism and has been shown to work well for single relaxation fluids such as worm-like micelles.\(^{45}\) For a majority of complex fluids, the underlying fluid structure relaxes *via* several mechanisms each having a characteristic relaxation time. However, the Maxwell model is still able estimate the dominant or terminal relaxation time.\(^{46}\)

For a more detail description of the relaxation spectrum one must consider more complicated models. By allowing the storage and relaxation elements in the model *ad infinitum*, a continuous Voigt-Kelvin model is introduced as follows\(^{33, 47}\)

\[ J(t) = J_g + \int_{-\infty}^{\infty} L \left( 1 - e^{-\tau / \tau_e} \right) d \ln \tau + \frac{t}{\eta_0} \]

where \(J_g\) is the instantaneous (or glass) compliance and \(L(\tau)\) is the retardation spectrum. Application of this approach to real data requires a discretization scheme, which is typically chosen to be logarithmic in nature to account for the largely varying time scales under consideration,

\[ J(t) = J_g + \Delta \tau \sum_{n=1}^{N} L_n \left( 1 - e^{-\tau / \tau_e} \right) + \frac{t}{\eta_0}. \] (2.55)
In practice, use of equation (2.55) is still highly susceptible to small experimental errors, where the best fit case often yields large discontinuities in the retardation spectrum. Problems of this type (i.e., Fredholm integrals of the first kind) are called ill-posed problems and require additional information that restricts the determined fitting parameters to realistic values. The \textit{a priori} constraint in this case is the expectation that the retardation spectrum is smooth or at least continuous. The numerical method employing this smoothness criterion is called Tikhonov regularization.\textsuperscript{48} Tikhonov regularization attempts to minimize the following function

\[
\text{SSE} = \left[ J(t) - J^{\text{expt}}(t) \right]^2 + \lambda \frac{\partial^2 L}{\partial \tau^2},
\]

where the squared-difference term represents the “goodness of fit” and the second derivative term accounts for the smoothness constraint. The parameter $\lambda$ determines the relative weighting of the goodness of fit versus the retardation spectrum smoothness. Finding an unbiased value for $\lambda$ is often the most difficult part of the algorithm. The algorithm used in the present work is based on a Tikhonov regularization scheme developed by Weese, which allows for a non-linear model, as in equation (2.55), and uses a self-consistent method of determining $\lambda$.\textsuperscript{49,50}

Once an adequate fit of the data is obtained, equation (2.55) is readily transformed into the frequency space as

\[
J^* = i\omega J(\omega) = J_g + \Delta_\tau \sum_{n=1}^{N} \frac{L_n}{(1 + i\omega \tau_n)} + \frac{1}{i\omega \eta_0}
\]

with the real and imaginary parts given by

\[
J' = J_g + \Delta_\tau \sum_{n=1}^{N} \frac{L_n}{(1 + \omega^2 \tau_n^2)} \text{ and } J'' = \Delta_\tau \sum_{n=1}^{N} \frac{L_n \omega \tau_n}{(1 + \omega^2 \tau_n^2)} + \frac{1}{\omega \eta_0}.
\]

Any linear viscoelastic function can be found using equation (2.54). Furthermore, since the creep compliance is directly related to the mean square displacement, this analytic expression also allows for the calculation of non-viscoelastic functions such as the time-dependent diffusion coefficient, the temporal scaling parameter (i.e., $\frac{d\ln \Delta r^2(t)}{dt}$), and the velocity autocorrelation function.
References


40. Faddeeva, V. N. & Terent'ev, N. N. *Tables of values of the function w(z) = exp(-z^2)/(1+2i/sqrt(pi)*int(0,z,exp(t^2),t) ) for complex arguments* (Pergamon Press, New York, 1961).


CHAPTER 3

Pluronic L64

L64 is a member of the BASF Pluronic family of poly(ethylene oxide) based tri-block copolymers. These macromolecular surfactants can be synthesized in diverse chemical and size regimes, leading to rich structural and dynamical behavior when dispersed in aqueous solution. In general, Pluronic-type macromolecular surfactants self-assemble into spherical micelles at sufficiently low concentration. Further increases in concentration can yield elongated micelles or even lamellae depending on the system temperature. At sufficiently high concentration soft gels can be formed from spherical micelles or lamellae. Aqueous L64 solutions are soft fragile systems where subtle elastic modes are often disrupted by mechanical perturbation. This susceptibility makes L64 an excellent candidate for probe particle thermal excitation studies via diffusing wave spectroscopy to investigate the underlying quiescent dynamics as external perturbations are not present.

3.1 Introduction

Pluronic L64, also known as Poloxamer 184, has the chemical formula \((\text{EO})_{13}(\text{PO})_{30}(\text{EO})_{13}\), where EO and PO denote ethylene oxide and propylene oxide respectively. PEO and PPO homopolymers exhibit lower critical solution temperatures (LCST) where the LCST for PPO is lower than the LCST for PEO.\(^1\)\(^2\) For PEO-PPO-PEO triblock copolymers, the disparity in lower consolute temperatures between blocks gives rise to a critical micellization temperature (CMT).\(^3\)\(^6\) In contrast to other non-ionic surfactants, Pluronics have a rather broad temperature range of micellization owing to size and composition polydispersity.\(^7\) The Pluronic micelle can be viewed as a PPO core surrounded by a corona of PEO arms. The relatively short PEO blocks are not large enough to entangle with PEO blocks of other micelles. It has been suggested that PEO blocks containing 10 or more EO units exhibit a partial helical confirmation; the preservation of this preferable confirmation leads to a repulsive stabilizing interaction between micelles.\(^8\)\(^9\) As the system temperature is increased beyond the CMT, water becomes a less favorable solvent for the PEO block thereby diminishing the strong repulsive inter-micellar interactions. At sufficiently high temperatures it has been proposed that the micelle-micelle interactions begin to resemble those predicted for sticky hard spheres.\(^10\)
3.2 Experimental Methods and Results

In the following subsection, we explore the structural and dynamical phase behavior of L64 as a function of both temperature and concentration. The general phase behavior is determined from cloud point and static light scattering measurements. Next, a general survey of the system’s response to an external perturbation is examined using steady shear viscosity. Finally, the high frequency response of the quiescent system is probed via diffusing wave spectroscopy measurements of probe particle thermal excitation with these thermal motions being analyzed in great detail.

3.2.1 Sample Information and Preparation

All samples of L64 were kindly donated by BASF. The solutions investigated in these studies were prepared from the same polymer lot number to minimize sample-to-sample variation. Such commercial products are expected to contain impurities as well as a size and compositional distribution. Researchers can take two avenues when exploring the physical properties of such a system: they can purify the material to facilitate the understanding of the basic parts or they can work with the material as received. The former case is beneficial in deconvoluting the effect of each component. In the latter case, the material is analyzed in the form that it will most likely be used in application. Additionally the majority of structural studies in literature use the material without modification, and for the sake of comparison, all studies performed herein will utilize the material as received.

Aqueous samples were made gravimetrically within 0.1% of the target concentration. The samples were stored at 6°C under constant agitation by a rotating plate to assist dispersion of the polymer. For DWS experiments, size certified polystyrene sphere standards were obtained from Molecular Probes (formally IDC Microspheres). The spheres come suspended in D.I. water and are charge stabilized with covalently bound surface sulfonate groups. Upon receipt, the standards were stored at 6°C to prevent microbial degradation of the spheres. The spheres were then added to the samples at least one week prior to experimentation to ensure complete and uniform colloidal probe dispersion.

3.2.2 90° Static Light Scattering

Static light scattering (SLS) has been used to probe the structure of several Pluronic aqueous solutions. SLS experiments were conducted with an eighteen fixed detector light scattering photometer (Wyatt Technology, Dawn EOS) with a 690 nm laser, which provides an
accessible scattering vector range of $q \sim 4.8 \times 10^{-4}$ to $q \sim 2.3 \times 10^{-3}$ Å$^{-1}$. The majority of samples showed a fairly angle independent scattering profile, as observed in similar SLS studies on Pluronics.$^{11,13}$ At low scattering angles the intensity increases, indicating the presence of larger size-scale structure. However, an investigation of a similar Pluronic system comparing SLS to ultra-small angle neutron scattering (USANS) concluded that the large-scale structure is most likely due to ‘dust’ (i.e., insoluble matter intrinsic to the polymer material).$^{16}$ Static light scattering is well-known to be susceptible to dust contamination making this technique particularly difficult to use on a commercial product such as L64. To remedy this situation one can either attempt to remove the dust by filtration or centrifugation or only consider scattering vectors outside the size-scale of the presumed dust. The former has been shown to alter the sample makeup by eliminating so-called impurities in the form of PEO-PPO diblocks and PPO homopolymer, which make up as much as 12% of the commercial product.$^{17}$ Since we set out to characterize the bulk commercial product, the latter strategy was adopted.

For the majority of the samples considered, the scattering profile is relatively flat and linear from $45^\circ$ to $135^\circ$. With the assumption that the scattering profile is relatively angle independent (i.e., the $90^\circ$ scattering is essentially the same as the zero angle scattering), the excess Rayleigh ratio at $90^\circ$ is related to the inverse osmotic compressibility as$^{13}$

$$\left(\frac{\partial \pi}{\partial c}\right)_{T,P} = \frac{Kc}{R_\theta} \left|_{\theta=0} \right. RT \approx \frac{Kc}{R_\theta} \left|_{\theta=90^\circ} \right. RT,$$

where $R_\theta$ denotes the Rayleigh ratio, $\pi$ is the solution osmotic pressure, $c$ is the solution concentration and $K$ is an optical constant. The inverse osmotic compressibility can be viewed as a solution’s resistance to concentration fluctuations.
Figure 3.1  Estimated inverse osmotic compressibility for L64 as a function of temperature. The dashed line is drawn in as a reference to the end of the micellization transition. The two linear sections are fit with a zero slope and standard linear regression, respectively.

In Figure 3.1 the measured temperature variation of the inverse osmotic compressibility is plotted for concentrations of up to 35 wt% L64 in water. To the left of the dashed line, it is difficult to recognize a pattern as the system is known to undergo a unimer-to-micelle transition. To the right of the dashed line there appears to be a flat region for temperatures up to $\sim 35°C$. For higher temperatures, the data shows an approximately exponential decrease in the inverse osmotic compressibility. It should be noted that the lines are used only to delineate regions of differing behavior.

The apparently incoherent pattern of $(\partial \pi / \partial c)_{T,P}$ at low temperatures and concentrations (to the left of the dashed line) is the result of two processes. The first process corresponds to the free L64 molecules collaboratively forming micelles, denoted as the unimer-to-micelle transition. The second process is due to the presence of low temperature, large length-scale aggregates. These aggregates are the source of “anomalous micellization” recognized in early literature.

As mentioned in the introduction, the unimer-to-micelle transition is known to occur over a fairly wide temperature range owing to size and composition polydispersity. The onset of micellization is known to occur at temperatures less than 20°C for all the concentrations considered here; thus the dashed line represents the offset temperature of micellization. Its linear concentration dependence is in excellent agreement with other studies on similar Pluronics.
Early claims in the literature of little or no micellar formation in aqueous Pluronic systems, was mainly attributed to large length-scale aggregates found at low temperatures.\textsuperscript{21-23} It is now well-known that these aggregates are composed of free PPO homopolymer and PEO-PPO diblocks. In particular the 1,750 g/mol PPO homopolymer is not soluble at 20°C. Presumably, the PEO-PPO diblock and Pluronic act as non-ionic surfactants to stabilize the solution. The length-scale of the aggregates is on the order of the wavelength of light as evidenced by images in Figure 3.2. There is a clear correspondence between the image shown in Figure 3.2 and the measured drop in inverse osmotic compressibility shown in Figure 3.1 by upside-down triangle at 20°C.

![Figure 3.2 Demonstration of large aggregates found in L64 at 20°C for 15 wt%, 20 wt%, and 25 wt% L64, from left to right. A He-Ne laser is used to highlight the aggregates.](image)

Interestingly, the 20 wt% L64 sample does not exhibit scattering at the bracketing temperatures of 15 and 25°C. Likewise, the 10 wt% L64 has a pronounced increase in scattering intensity at a temperature of 25°C, which is bracketed by lower scattering intensity at 20 and 30°C. This indicates that each sample concentration should display a similar narrow temperature band of aggregation with the onset temperature decreasing with increasing concentration. It should be noted that results to the left of the dashed line in Figure 3.1 are only qualitatively related to the inverse osmotic compressibility. For these samples, Equation (3.1) is not applicable since there is an apparent upturn in the lower scattering angle intensity that is not explained by dust. The Rayleigh ratio at zero angle is therefore under predicted by the 90° quantity, and the actual inverse osmotic compressibility would be even smaller.

The first linear region in Figure 3.1 is temperature independent, as expected for a good solvent.\textsuperscript{24} At temperatures higher than approximately 35°C, $(\partial \pi / \partial c)_{T,P}$ begins to decrease exponentially, corresponding to a decrease in the repulsive interactions between micelles. At the lowest concentrations ($c \sim 10$ wt%), the decrease is no longer well described by an exponential; this most likely owes to the fact that the osmotic compressibility diverges as the system approaches phase separation.\textsuperscript{25, 26} Low concentration phase separation is consistent with cloud point measurements shown below in Figure 3.3.
The phase separation is driven by the dehydration of the PEO arms that stabilize the micelle. The micelles are hypothesized to interact as hard spheres; however, this assumption breaks down at higher temperatures. In addition, the steric stabilization decreases and the potential between micelles becomes “sticky”.\textsuperscript{10, 27, 28} An attractive potential increases the likelihood that two micelles will be in the immediate vicinity of each other, which favors large concentration fluctuations and results in a decrease of the observed inverse osmotic compressibility.\textsuperscript{29} This is consistent with small angle neutron scattering (SANS) experiments performed by Lobry \textit{et al.}\textsuperscript{10} where the so-called stickiness parameter was shown to increase at 35°C for 20 wt% L64 in D$_2$O.

3.2.3 Bulk Viscosity Measurements

Bulk viscosity measurements were made with a TA AR2000 stress controlled rheometer using a concentric cylinder geometry. The steady flow viscosity was determined for concentrations of 5 to 40 wt% L64 using a temperature ramp of 0.5 °C/minute; the selected ramp rate was chosen since slower ramp rates gave similar results. Selection of the measurement stress was based on a stress sweep where a stress-independent “flat” region was identified. A thin layer of low viscosity poly(dimethyl siloxane) (PDMS) oil was added at the air-solution interface to reduce water evaporation from the sample. Samples with and without the PDMS overlay exhibited the same viscosity within experimental error. Each temperature ramp was repeated twice on the same sample to confirm that PDMS uptake was not an additional factor affecting the viscosity determination.
Figure 3.4  Temperature ramp bulk viscosity measurements for concentration of 5 to 40 wt% L64 (only every fifth datum point is plotted for clarity). Literature values for water are represented by the solid black line.30

Figure 3.4 shows the bulk viscosity traces for eight concentrations of L64 as a function of temperature. The two lowest concentrations, 5 and 10 wt%, exhibit slight undulations owing to the low viscosity inertial compensation of the rheometer. In general, the low concentration data follow the same viscosity diminution with increasing temperature as water indicating that, although there is some enhancement due to the micelles, the solution viscosity is dominated by the underlying solvent. There is a slight change in the slope most noticeable for intermediate concentrations at low temperature, essentially corresponding to the dashed line given in the inverse osmotic compressibility data (Figure 3.1). As previously mentioned this is the unimer-to-micelle offset temperature above which micellar dynamics begin to markedly influence the solution viscosity.

An interesting result obtained from SANS is that the micellar volume fraction is relatively unaffected by temperature.28 However, the data in Figure 3.4 shows the viscosity for intermediate to high concentrations deviates from the trend of the underlying solvent. This is in contradiction to what is expected for non-interacting hard spheres. It is hypothesized that the micellar interactions must therefore possess qualities beyond the non-interacting hard sphere model and that these interactions
are strongly influenced by temperature, an observation that will be discussed further in the following sub-sections.

The most notable feature in Figure 3.4 is the dramatic increase in viscosity at low concentrations upon increasing temperature. This is congruent with the SLS measurements, showing amplified concentration fluctuations that ultimately diverge at the cloud point. These fluctuations play a critical role in the evolution of dynamical modes leading to an enhanced apparent viscosity. In the next section, DWS measurements of probe sphere thermal excitation will provide access to the fluctuation time-scale set by the underlying micellar dynamics. Through this technique, the superposition of dynamical processes from high frequencies to the observed long-time behavior that is revealed in the steady shear measurements is explored.

### 3.2.4 Probe Particle Dynamics in L64

Polystyrene spheres (420 nm diameter) were dispersed in L64 solutions at 0.5 wt%. This concentration is sufficient to ensure multiple scattering yet small enough to neglect hydrodynamic interactions between spheres. The dynamics of the dispersed colloidal spheres were measured with transmission mode DWS in the high temperature cell as described in Chapter 1.

One of the main advantages of DWS is its resolution of dynamics at extremely small time-scales. Furthermore, dynamics are determined over several time decades, allowing study of multiple relaxation processes and their temporal scaling. In the majority of samples the longest relaxation time was accessible to DWS, allowing the zero frequency (shear) viscosity, \( \eta_0 \), to be extracted from the measured colloidal sphere mean square displacement via the Stokes-Einstein relation,

\[
\langle \Delta r^2(t) \rangle = \frac{k_B T}{\pi a \eta_0} t.
\]

The viscosity values were obtained by fitting the long-time mean square displacement, where the temporal scaling was required to be diffusive (\( \langle \Delta r^2(t) \rangle \sim t^\alpha \) where \( \alpha = 1.00 \pm 0.05 \)). For the low concentrations at 50 and 55°C the scaling of the mean square displacement was found to be sub-diffusive, (\( i.e., \alpha < 1 \)), at the longest time-scale considered. Figure 3.5 compares the viscosity determined from the colloidal sphere thermal motion with conventional steady shear viscometry.
Figure 3.5 Bulk mechanical steady shear viscosity, $\eta$, measurement and zero frequency viscosity, $\eta_0$, obtained from diffusing wave spectroscopy for different concentrations.

In general, both the steady shear viscosity and DWS zero frequency viscosity are in good agreement. The values determined from DWS, however, are consistently smaller than the values given by bulk measurements. There are several possible reasons for this systematic discrepancy. First, probe particle thermal excitations occur over a distribution of strains far smaller than normally attainable by mechanical perturbation. Such mechanically applied shear stresses can organize fragile systems thereby slightly enhancing flow resistance. However, shear thickening, or dilatancy, is usually only observed at high strain rates (i.e., for $\text{Pe} = \dot{\gamma} a^2/D_0 \gg 1$) and produces shear rate dependent behavior not observed in stress sweep measurements. Second, a depletion layer may exist near the sphere surface such that this local viscosity is reduced in comparison with that of the bulk. Finally, the discrepancy may simply owe to the physical parameter estimates used in the $l'$ calculation, which may contain error (see Chapter 1). In any case, with the exception of the 55°C data, the values are within 20% relative error.
The bulk viscosity given in Figure 3.4 reflects the limiting behavior of the mean square displacement at long times; it does not provide information on how the L64 solution dynamics ultimately evolved to this long-time value. The data presented below in Figure 3.6 demonstrate that the mean square displacement ultimately exhibits the diffusive scaling from which the zero shear viscosity is obtained. More importantly, the full temporal evolution of the mean square displacement contains information regarding the viscoelastic nature of these fluids.

Figure 3.6  Mean square displacement traces for L64 concentrations at 20°C (top) and 50°C (bottom)
The Brownian particle mean square displacement temporal behavior illustrated in the upper panel of Figure 3.6 is that expected for a simple viscous fluid. Upon careful inspection, slightly sub-diffusive early-time motion is apparent for the 40 wt% solution. Both panels clearly indicate (i) short-time sub-diffusive behavior owing to viscoelasticity at the highest concentrations and (ii) short-time super-diffusive behavior due to probe particle hydrodynamics at the lowest concentrations. The short-time dynamics are more apparent in the 50°C data (bottom panel) where it becomes evident that early-time elastic storage (high frequency elasticity) underlies the higher viscosity observed in the bulk measurements.

In order to compare mean square displacement behavior at different temperatures, temporal traces must be scaled for the effect of thermal energy. This is achieved by recalling the earlier definition of the microscopic creep (see Chapter 2)

\[ J_a(t) = \frac{\pi a}{k_B T} \{ \Delta r^2(t) \} . \]

Here, the probe size scaling is also readily apparent. Assuming the generalized Stokes-Einstein relationship is valid, this expression reduces to the bulk creep compliance.

The microscopic creep is shown in Figure 3.7 for six concentrations and over a range of temperatures below the cloud point. Data for temperatures lower than the offset micellization temperature are not shown for clarity; in general, they demonstrate purely diffusive behavior with a lower microscopic creep. Eventually the short-time microscopic creep converges with the values found at higher temperatures upon reaching the offset micellization temperature.

Beginning with the lowest concentration, one finds that the microscopic creep collapses to a single curve at sufficiently short time. In this limit, the data display super-diffusive behavior associated with early-time probe particle hydrodynamics, as recognized in the above mean square displacement traces. At later times, the microscopic creep trace begins to deviate from purely viscous behavior at the highest temperatures considered. This viscoelastic behavior is amplified as the concentration increases with the onset of viscoelastic behavior occurring at even shorter times. At a concentration of 30 wt% the microscopic creep still appears to converge at the shortest length and time-scales considered in this study.

---

1 Such super-diffusive behavior is due to the induced self-hydrodynamic flow of the probe particle at early times. This is not a dynamical effect of the system, but rather a general artifact of probe particle motion at time-scales \( \propto a^2 / \eta \). See §2.4 of Chapter 2 for details.
Figure 3.7 Comparison of the microscopic creep for 6 concentrations: (a) 5 wt%, (b) 10 wt%, (c) 15 wt%, (d) 20 wt%, (e) 25 wt%, and (f) 30 wt% over a range of temperatures above the offset micellization temperature to 57°C (only every third datum point is shown for clarity).
A particularly striking observation is the collapse of the early-time dynamics to a single curve demonstrating a nearly temperature independent high frequency viscosity for temperatures greater than the unimer-to-micelle offset temperature. Figure 3.8 compares the high frequency viscosity, $\eta'_\infty$, extracted from the short-time diffusive region with the bulk viscosity, $\eta$, determined from mechanical rheometry. For temperatures below the unimer-to-micelle transition (not shown in Figure 3.7) there is a decrease in viscosity with increasing temperature. Both the high frequency viscosity and bulk measurement track well with the underlying behavior of the solvent, as noted earlier in subsection 3.2.3. At the unimer-to-micelle offset temperature, the high frequency viscosity locks into a value showing very weak to no temperature dependence. SANS data obtained by Liao et al. also indicate the micelle volume fraction is independent of temperature.\textsuperscript{28} This is consistent with the picture put forth by Batchelor where the high frequency viscosity is only a function of hydrodynamics.\textsuperscript{33}

![Graph showing viscosity measurements](image)

**Figure 3.8** Bulk viscosity measurements, $\eta$, compared to the high frequency viscosity, $\eta'_\infty$, as obtained from DWS ($\beta$-spline fit is given to guide the eye).

All concentrations represented in Figure 3.7 have similar characteristics. At low temperatures the microscopic creep scales diffusively with a magnitude dictated by the high frequency viscosity. Upon
increasing temperature, there is an accretion of frequency dependent elasticity dividing short and long
time diffusive regimes. The bifurcation of the steady shear viscosity from the high frequency viscosity
shown in Figure 3.8 is due to the additional concatenation of elasticity originating from micellar
Brownian dynamics and inter-micellar interactions.

3.3 Discussion

In the following subsections, possible mechanisms underlying the observed microscopic creep are
discussed. First, we analyze the micelles as hard spheres undergoing Brownian motion where energy
storage results from perturbing the equilibrium micelle configuration. Next, the possible role played
by temperature dependent attractive inter-micellar interactions is considered. Finally, possible
discrepancies between this system and an attractive hard sphere dispersion are considered thereby
leading to other possible dynamical processes that may yield the observed phenomenon.

3.3.1 Viscoelasticity in Dispersion of Hard Spheres

The simplest model of micellar interactions is that of hard spheres, where excluded volume
interactions constrain the configurational freedom of the dispersion. Brownian motion leads to spatial
fluctuations about the equilibrium configuration. Regions of locally enhanced sphere concentration
have an increased likelihood of unfavorable excluded volume encounters. Brownian motion ultimately
disperses the micelles towards the equilibrium configuration. This mechanism is an illustration of the
fluctuation-dissipation theorem and describes undulations in the free energy landscape corresponding
to energy storage and relaxation. The larger the concentration fluctuations, the greater the amplitude
of these undulations, corresponding to frequency dependent elasticity.33-35

The embedded probe particle size is orders of magnitude larger than the micelle size. The thermal
excitation of embedded probe particle stimulates a commensurately large response by perturbing the
equilibrium micellar configuration. Well within the linear response regime, probe particle motion
excites elastic modes, as described within the fluctuation-dissipation framework. The material
acquiesces to its low equilibrium free energy state on a time-scale set by micellar Brownian dynamics.
To examine this effect in detail, the microscopic creep is converted to the complex viscosity, and
further decomposed into its real and imaginary components. This is performed by fitting the data to
the Voigt-Kelvin model for a viscoelastic liquid using Tirkhonov regularization.36-39 (see Appendix
2.E.b of Chapter 2)
Equation (3.2) provides an analytic form that is straightforward to transform into the Fourier domain allowing for the separation of real and complex components.

\[ i\omega J_n^\prime (\omega) = J_n^{\prime \prime} (\omega) = J_n^\prime (\omega) - iJ_n^{\prime \prime} (\omega) \]

These components are transformed to the loss, \( \eta' \), and storage, \( \eta'' \), moduli of the complex viscosity through the following relationship:

\[
\eta' (\omega) = \frac{1}{\omega} \frac{J'' (\omega)}{J'^2 (\omega) + J''^2 (\omega)} \quad \eta'' (\omega) = \frac{1}{\omega} \frac{J' (\omega)}{J'^2 (\omega) + J''^2 (\omega)}.
\]

(3.3)

The zero and high frequency viscosities demarcate the bounds of these functions, providing a vehicle for normalization. The components of the normalized complex viscosity are plotted for 25 wt% L64 solutions at high temperatures in Figure 3.9.
The complex viscosity high frequency scaling for a concentrated colloidal dispersion is determined by the strength of the repulsive interactions. The rheological behavior of sterically stabilized silica sphere dispersions measured by van der Werff and de Kruif showed that both the real and imaginary components of the complex viscosity are expected to scale as \( \omega^{-1/2} \), which is consistent with a free draining model put forth by Brady\(^\text{35}\). In contrast, Shikata and Pearson\(^\text{40}\) examined the high frequency behavior of indexed matched silica sphere dispersions where the storage component exhibited \( \omega^{-1} \) scaling. Lionberger and Russel\(^\text{41}\) reconciled the differences by arguing that lubrication forces must be included for true hard sphere interactions, which cause the storage component of the complex viscosity to scale as \( \omega^{-1} \). Apparently, the steric coating used by van der Werff and de Kruif contributes significantly to the high frequency behavior, indicating its sensitivity to near-contact interactions.

In the present work, the high frequency scaling is \( (\eta'(\omega) - \eta'_\infty) \sim \omega^{-3/4} \) and \( \eta''(\omega) \sim \omega^{-0.58} \). It should be noted that \( \eta'(\omega) \) begins to decrease faster than the \(-3/4\) scaling, approaching the end of the decay; however, in this region the data becomes suspect due to possible errors in the domain transform of the Voigt-Kelvin decomposition. The high frequency scaling behavior indicates micellar interactions beyond hard sphere interactions, as also concluded from the inverse osmotic compressibility measurements. Furthermore, \( \eta''(\omega) \) contains other dynamic processes that contribute to an observed variation in frequency scaling. The broad distribution of the relaxation processes is evident from the maximum in the storage component occurring at values less than \( 0.5(\eta'_\infty(\omega) - \eta'_\infty) \), which is the anticipated value for a single relaxation process.\(^\text{34}\) While the onset of elasticity is not simply explained by hard sphere interactions, the low frequency scaling \( (\eta''(\omega) \sim \omega^j) \) is identical to that predicted for the relaxation of concentrated hard spheres.\(^\text{35}\)

To identify mechanisms contributing to the deviation of high frequency scaling from that expected for hard spheres, we turn our attention to the absence of low temperature sub-diffusive behavior. SANS experiments reveal a rather insensitive high \( q \) (small length-scale structural) response to changes in temperature.\(^\text{28}\) However, temperature significantly affects the low \( q \) range, in agreement with our SLS data, primarily influencing the structure factor. Therefore, temperature dependent inter-micellar interactions are responsible for changes in the observed dynamic and structural properties.

As previously speculated, the micelles do not exist as well-defined hard spheres. The sterically stabilizing PEO arms extending from the micelle core significantly ‘soften’ the hard sphere potential. For example, studies on hard spheres with a relatively small steric layer, \( \sim 1/20 \) of the radius, yields a softening of the inter-particle potential that produces large changes in the hard sphere crystallization phase boundary.\(^\text{42}\) In comparison, the corona of an L64 micelle is typically \( 1/4 \) the size
of its core. It is possible that the PEO arms act as a dampener, preventing large fluctuations in micelle concentration and thwarting the development of elasticity. The solvent quality of PEO in water decreases with increasing temperature. This simply implies that there is an increased likelihood of PEO-PEO contacts. Consequently, the PEO chains in the corona will contract, yielding a stiffer spring. More importantly, PEO chains from neighboring micelles have an increased likelihood of interacting, producing a slightly ‘sticky’ potential.

### 3.3.2 Adhesive Hard Sphere Model and Percolation

In 1968, Baxter analytically solved the Ornstein-Zernike equation for a square-well potential in the limit of decreasing well width using the Percus-Yevick approximation. This solution brings in an additional single ‘stickiness’ parameter, $1/\tau$, to the hard sphere model, encompassing the strength of the attractive square well potential. Lobry et al. employed this sticky or adhesive hard sphere (AHS) potential in structure factor calculations that ultimately were found to be in good agreement with L64 SANS data. In agreement with solvent quality arguments, this analysis demonstrated that inter-micellar interactions become more attractive with increasing temperature. Attraction between micelles leads to a decrease in the inverse osmotic compressibility and explains the sharp increase in viscosity. Micelle aggregation into clusters is an inherent consequence of the AHS potential. For a given temporal snapshot of the micellar configuration, two or more micelles interacting through an AHS potential constitutes a dynamic cluster. That is, the constituent micelles are in dynamic equilibrium, constantly forming clusters and breaking apart. The lifetime of a cluster is a function of the stickiness parameter describing the attractive interaction. Increasing stickiness leads to an increasing probability that several micelles will exist in a single cluster. This naturally leads to a percolation threshold where micelle clusters span the entire sample volume. More precisely, the AHS model predicts a percolation threshold beginning at the cloud point and crossing the phase diagram to lower concentrations and high temperatures.

---

‡ This is true of AHS particles with an inverse solubility, or LCST behavior. In the case of an upper consolute temperature, the percolation threshold is predicted to begin from the critical point and extends to higher concentrations and temperatures (e.g., see Chiew & Glandt 1983, Verduin & Dhont 1995, or Miller & Frenkel 2004).
Figure 3.10  $1/\tau$-$\phi$ phase diagram predicted for the Baxter adhesive hard spheres exhibiting LCST behavior (adapted from reference 47). The values along the ordinate represent increasing “stickiness” relative to the critical stickiness, $1/\tau_c = 10.25$, predicted from theory. The abscissa is the volume fraction of spheres (see reference 48 for a more fastidious calculation).

The mechanically defined percolation threshold is a transition from a fluid sol to an elastic gel brought about by clusters spanning the sample volume. The microscopic creep in Figure 3.7 shows slight sample elasticity, but is clearly not gel-like (i.e., solid-like), as indicated by the viscous escape. The data given in reference 10 by Lobry et al. shows a viscous dominated mechanical response for all temperatures and time-scales considered. While this is in apparent contradiction to their conclusion of L64 having AHS driven percolation, they essentially redefine the percolation threshold as a sharp increase in the elastic modulus, which happens to be less than the viscous modulus.

The defined percolation threshold is incomplete as it attempts to paint a picture of a sol-to-gel transition without mentioning the time-scale, hence we further distinguish between a static and dynamic percolation threshold. Static percolation does not evolve in time. The spanning cluster is more or less permanent as in the case for an irreversible gel. Dynamic percolation involves a spanning cluster that is constantly evolving. This provides an additional mechanism for long time relaxation ultimately allowing for a viscous escape. Static and dynamic percolation thresholds both contain the essential percolation feature of a spanning cluster. However, a dynamic percolation threshold is only gel-like on the time-scale set by the lifetime of a spanning cluster.
In order for two micelles to interact through the AHS potential, they must diffuse from their equilibrium configuration to close vicinity of one another. Therefore, the time-scale of a collective string of micelles spanning the sample volume is the time-scale of Brownian motion ($\sim a^2/D_0$). The crossover from viscous to elastic behavior associated with a percolation threshold occurs well below the time-scales attainable by traditional mechanical measurements. Once a single micelle breaks from the collective string, the string no longer spans the sample volume. For that reason, the elastic dominated behavior at the percolation threshold is expected to be short-lived.\textsuperscript{48}

As established, increasing temperature increases the strength of the attractive potential between micelles. Using temperature as a control variable, DWS tracer studies are well suited for high frequency exploration of dynamical shifts corresponding to the presumed amalgamation of micelles into clusters. The elastic and viscous moduli related to stress relaxation are found using the aforementioned Voigt-Kelvin decomposition of the microscopic creep with the recognition that $G'(\omega) = \omega \eta''(\omega)$ and $G''(\omega) = \omega \eta'(\omega)$ (see Equations (3.2) and (3.3)). In the figure below (Figure 3.11), the elastic modulus is observed to increase with increasing temperature.
At the highest temperature considered, the elastic modulus crosses the viscous modulus at $\omega \sim 10^5$ rad/sec, which is well beyond the capabilities of mechanical rheometry thereby signifying a short-lived elastic solid as detected by DWS. Interestingly, the elastic modulus crossover occurs on the verge of the system entering the two-phase region. This suggests that increasing the attractive potential promotes micellar concentration fluctuations, which manifests ever-increasing elasticity and finally induces phase separation.
### 3.3.3 Beyond the Adhesive Hard Sphere Model

The behavior shown in Figure 3.11 is remarkably independent of concentration. Figure 3.12 illustrates a similarity in viscous-to-elastic transitions occurring at approximately the same time ($\omega_c \sim 8.5 \times 10^4 \text{ rad/s}$) and temperature ($T_c \sim 57^\circ C$) over a range of concentrations.

![Graph showing elastic and viscous moduli for a range of concentrations at the highest temperature considered (57°C). The inset shows the moduli scaled by $c^{-2}$.](image)

**Figure 3.12** Elastic and viscous moduli for a range of concentrations at the highest temperature considered (57°C). The inset shows the moduli scaled by $c^{-2}$.

The high frequency behavior is dictated solely by hydrodynamics and as such the modulus should scale with $c^{-2}$ as suggested by Brady (shown in the inset).[^35] Although a better ‘concentration’ variable might be the actual micellar volume fraction, SANS data reveal that the bulk concentration has a fairly linear relationship with micelle volume fraction up to $\sim 25$ wt% L64 in D$_2$O.[^28] The early-time hydrodynamics set the magnitude of the response, and the onset of Brownian and potential forces dictates the evolution of the response. The dynamical pathway shows a slight deviation at lower frequencies, as evident by the stratification in the elastic modulus. This indicates concentration mainly impacts the relaxation of the percolated network.
The percolation threshold temperature displays almost no concentration dependence. This is in apparent conflict with the AHS model, where the percolation threshold temperature decreases with increasing concentration (see Figure 3.10 with the realization that $\tau_c/\tau \sim T$). However, other experimental studies on ‘model’ AHS systems demonstrate an almost flat percolation threshold temperature ($\Delta T_{gel}/\Delta \phi < 1^\circ C/0.2$)\textsuperscript{49}, which is consistent with the present study.\textsuperscript{49, 50} These authors were able to directly compare the ‘stickiness’ parameter to theory and conclude their data show only qualitative agreement.

The AHS model does not specify the temperature dependence of the attractive potential. The steepness of the percolation threshold as it relates to the stickiness parameter (shown in Figure 3.10) is therefore unspecified. Several smaller-scale factors may come into play when considering intermicellar attraction. One could speculate that the dynamics of surfactant exchange between the micelles and the surrounding fluid plays a role in the location of the percolation threshold. Individual Pluronic molecules are not anchored to the micelles, but rather in a rapidly exchanging equilibrium with the surrounding unimers.\textsuperscript{51} Even in the theoretical limit of an infinite attractive potential, the Pluronic chains involved in an attractive bond can simply be extracted and replaced by free unimers with little consequence to the free energy of the system-especially on the time scales of interest here. Upon increasing temperature, however, the concentration of the free unimer decreases. The volume fraction of micelles does not change, but the concentration within the micelle increases, yielding a leaner surrounding solvent. Thus extracting a Pluronic molecule at higher temperatures has a greater free energy penalty.

Finally, it should be realized that the AHS model is an idealization of hard sphere excluded volume with an adhesive potential allowing for attractive interactions. In the Pluronic micelles studied here, the transition from a soft repulsive to an attractive interaction is facilitated by a change from good to poor solvent quality with regards to the PEO chains. It is unclear how the AHS potential allows for soft repulsion other than by an inflated volume fraction.

\subsection*{3.4 Conclusion}

These studies demonstrate the use of DWS microrheology to study the short-time dynamics of aqueous L64 solutions, revealing a temperature independent high frequency viscosity for temperatures larger than the micellization offset temperature. The evolution of the dynamics through elastic modes yields a long-time viscosity that is in very good agreement with steady shear viscosity measurements. A purely hard sphere interaction between micelles is found to be insufficient for accurately describing
the microscopic creep as the temperature is increased. The dynamics at high temperatures are dominated by an apparent attractive inter-micellar potential consistent with inverse osmotic pressure measurements.

In all probability, percolation as suggested by Lobry *et al.* occurs in the L64 system at sufficiently high temperatures. However, the alleged locus of a percolation threshold is more likely the system beginning to exhibit elastic modes at frequencies not accessible by a traditional mechanical rheometer. This exaggerates the likelihood of percolating structures occurring at lower temperatures and in turn presumes a greater dependence of the percolation threshold on concentration neither of which is observed in the microscopic creep measurements discussed here. Despite this, the AHS potential is qualitatively consistent with the results found here and we have confirmed the presence of a short-lived elastic gel at high temperatures, which we attribute to a spanning cluster indicating the crossing of the percolation threshold.
References


30. Watanabe, K. (The International Association for the Properties of Water and Steam, Vejle, Denmark, 2003).


CHAPTER 4

Pluronic P85

P85 is a member of the BASF Pluronic family of poly(ethylene oxide) based tri-block copolymers. P85 exhibits several unique characteristics that make this macromolecular surfactant a particularly appealing complex system for colloidal sphere thermal motion studies using diffusing wave spectroscopy (DWS). At low-to-moderate temperatures, single P85 molecules cooperatively form micelles, undergoing a unimer-to-micelle transition. For concentrations above 20 wt% in water at these temperatures, the micelles self-assemble into well-ordered micellar crystals. At higher temperatures, the micelles begin to elongate into rod-like objects thereby disrupting the crystalline structure and ultimately entangle. Micelle Brownian motion dictates the assembly dynamics and relaxation in Pluronic structures. The high frequency range of DWS is ideally suited to explore dynamic micellar structures while assuring access to the linear response regime.

Particularly interesting is the sensitivity of the micellar crystalline phase to hydrostatic pressure. Mortensen et al. used small angle neutron scattering (SANS) to observe so-called ‘Pressure-Induced Melting’ of a similar Pluronic micellar-crystal former, known as F88.\textsuperscript{1} Coupling transmission-mode DWS with a high-pressure scattering cell, the quiescent behavior of P85 solutions was investigated over a wide range of temperatures and pressures. In essence, dynamical pressure-temperature phase diagrams are accessible that provide insight into the connections between dynamic micellar structures and observed macroscopic properties.

4.1 Introduction

P85 is an oligomeric-sized ethylene oxide triblock macromer with an average molecular structure shown below.

\[
\text{HO} \underbrace{\text{CH}_2\text{CH}_2\text{O}}_{25} \underbrace{\text{CH}_3}_1 \underbrace{\text{CH}_2\text{CH}_2\text{O}}_{20} \underbrace{\text{CH}_2\text{CH}_2\text{O}}_{25} \text{H}
\]

The middle block contains pendent methyl groups that significantly affect the solubility of the poly(ethylene oxide) chain. At sufficiently low temperatures, Pluronic molecules exist as free chains or so-called unimers. At higher temperatures, the poly(propylene oxide) (PPO) middle block becomes
insoluble, and the unimers cooperatively self-assemble to form spherical micelles to minimize unfavorable PPO-water contacts. Owing to the broad size and composition distribution of the Pluronic molecules, the transition from unimer to micelle occurs over a fairly wide temperature range.²

\[
\text{Unimer} \xrightarrow{T} \text{Micelle}
\]

At sufficiently high concentration, the micelles interact with one another, thereby altering the sample bulk properties – sometimes quite dramatically. Using small angle neutron scattering (SANS) Mortensen and Pedersen demonstrated that P85 micelle-interactions are well-described by a hard sphere potential at low temperatures.³ At the so-called critical micelle volume fraction, long-range order is observed, which is indicative of a cubic paracrystalline phase.⁴-⁶ Application of shear aligns the crystalline domains yielding a single body-centered cubic (BCC) colloidal crystal.⁵, ⁷, ⁸

In the micellar phase, a significant portion of unimers exist in dynamic equilibrium with the micelles.⁹ As the temperature is increased, more unimers are incorporated into micelles. Once the maximal micellar volume fraction is reached, the unimers begin to displace latent water, effectively densifying the micelle.¹⁰ Although the volume fraction of micelles does not increase, there is an overall increase in the aggregation number of each micelle; in contrast to small molecule surfactants, Pluronic molecules are able to span the micelle shown pictorially in Figure 4.1.

![Figure 4.1. Sketch of a Pluronic micelle highlighting an individual PEO-PPO-PEO chain spanning the micellar core.](image)

The swelling of micelles at higher temperature causes an entropic strain, promoting axial growth.³ This entropically driven mechanism for shape change is consistent with depolarized dynamic light scattering measurements of Schillén, Brown, and Johnsen that indicate a transition from a spherical
to an elongated or rod-like morphology at elevated temperatures.\textsuperscript{11} In addition, several studies suggest that these rod-like micelles can be aligned into a hexagonal phase upon application of shear.\textsuperscript{7}

As previously mentioned, hydrostatic pressure also has a profound effect on the self-assembly of aqueous Pluronic systems. Aqueous Pluronic F88 was observed to have a high susceptibility to hydrostatic pressure. F88 is known to form a micellar cubic paracrystalline phase at moderate concentrations and temperatures.\textsuperscript{5} Mortensen \textit{et al.}\textsuperscript{1} used SANS to confirm the occurrence of an order-to-disorder transition upon increasing pressure; that is, increasing hydrostatic pressure essentially ‘melts’ the crystalline solid. The authors further assert the idea that Pluronics have a structural correspondence between temperature and pressure, meaning that there is an infinite set of temperature/pressure pairs with an equivalent structure. In the present work, we intend to contribute to the understanding of Pluronic behavior using DWS colloidal sphere thermal motion studies by examining the dynamical response of P85 aqueous solutions to changes in temperature and hydrostatic pressure.

\subsection{4.2 \textit{Experimental Methods}}

Numerous studies on aqueous Pluronic systems have uncovered novel morphologies by tuning temperature and concentration.\textsuperscript{12-16} DWS colloidal sphere thermal motion studies provide a distribution of dynamical information, allowing for the study of multiple relaxation processes and their temporal scaling; thus, these studies are well-suited for the exploration of Pluronic systems approaching structural and dynamical transitions. Utilizing a high-pressure scattering cell, originally designed for SANS experiments (see Chapter 1), P85 aqueous solution dynamics are investigated at temperatures ranging from 15 to 85°C and up to pressures of 210 MPa.

In general, DWS colloidal sphere thermal motion studies are conducted by embedding inert spherical probe-particles into the sample of interest. The probe particles’ scattering cross-section and concentration as well as the length of the scattering cell determines the spatial resolution of the measurements. In these studies 420 nm polystyrene spheres are dispersed in aqueous P85 samples at a concentration of 0.5 wt\%, providing nanometer displacement resolution; this sphere concentration also exhibits sufficient multiple scattering to insure the diffusive transport of light required for DWS.

Meaningful dynamic information is found from the correlations of light scattered from the colloidal spheres undergoing thermal motion. The measured autocorrelation functions are then numerically converted to their corresponding mean square displacements as a function of lag time, using a
procedure described in Chapter 1. The resulting mean square displacement is scaled with respect to thermal energy by conversion to the microscopic creep (see Chapter 2),

\[ J_a(t) = \frac{\pi a^2}{k_B T} \langle \Delta r^2(t) \rangle. \] (4.1)

Viscoelastic liquids exhibit a characteristic long-time diffusive limit (i.e., \( \sim t^1 \)) in their microscopic creep. It is oftentimes convenient to represent this limit as the zero frequency (or zero shear) viscosity using the following relationship

\[ \eta_0 = \lim_{t \to \infty} \left( \frac{d J_a(t)}{dt} \right)^{-1}. \] (4.2)

Aqueous P85 solutions of three different concentrations are examined to explore the effect of temperature and pressure on morphological transitions. At 5 wt\% P85, we focus on the unimer-to-micelle transition and further examine dynamical behavior at high temperature where we find a sphere-to-rod transition. At 25 wt\% P85, we examine the disorder-to-order transition as the micelles become increasingly crowded and finally undergo a predicted first order phase transition to a micellar crystal. Last, we probe samples of 35 wt\% P85 where we observe a significant micellar crystalline phase as well as a concentrated rod-like micelle phase. Variations of temperature and pressure allow capture of the essential elements of each morphology and attendant phase transitions.

### 4.2.1 Sample Information and Preparation

All samples of P85 were kindly donated by BASF and used as received. As in the previous chapter, solutions of P85 were prepared from the same polymer lot number to minimize sample-to-sample variation. Aqueous samples were made gravimetrically within 0.1\% of the target concentration. The samples were stored at 6°C under constant agitation by a rotating plate to assist in dispersion of the polymer. For DWS experiments, size-certified polystyrene sphere standards were obtained from Molecular Probes (formally IDC Microspheres). The spheres come suspended in D.I. water and are charge stabilized with covalently bound surface sulfonate groups. Upon receipt, the sphere standards were stored at 6°C to prevent microbial degradation of the spheres. The spheres were subsequently added to the samples at least one week prior to experimentation to ensure complete and uniform colloidal probe dispersion.
4.3 Unimer-to-micelle Transition, 5 wt% P85

DWS was used to measure colloidal sphere thermal motion in a 5 wt% P85 aqueous solution in order to investigate the unimer-to-micelle transition dynamically. Figure 4.2 shows the microscopic creep of 420 nm diameter polystyrene spheres in a 5 wt% P85 sample.

Figure 4.2 The microscopic creep for 5 wt% P85 in water at ambient pressure over a range of temperatures. The inset shows the comparison of the viscosity obtained by fitting the data (see Equation (4.2)) and the literature values for water.

The microscopic creep displays diffusive scaling for temperatures below 70°C. Early-time super-diffusive scaling is not an intrinsic property of the sample but rather an artifact of probe hydrodynamics (see Chapter 2). The semi-log plot (inset) compares the zero frequency viscosity, found using Equation (4.2), to the literature values for the viscosity of water. Between 20 and 40°C, there is a slight change in slope relative to water, which is associated with the conversion of unimers...
to micelles. This observed decrease in solution viscosity can be explained through the Einstein equation for the viscosity, $\eta$, of dilute non-interacting spheres,

$$\eta = \eta_s \left(1 + \frac{5}{2} \phi \right),$$

where $\eta_s$ is the solvent viscosity and $\phi$ is the hard sphere volume fraction. The solvent viscosity is a function of the free unimer concentration and temperature, and the micellar or hard sphere volume fraction is also a function of these two factors as the volume fraction increases with temperature. Thus, there are two opposing effects present in the observed viscosity during the unimer-to-micelle transition: (i) the dilution of the solvent by loss of unimer, which decreases $\eta_s$, and (ii) the resulting micellar volume fraction increase with increasing temperature, which increases $\phi$. As shown in the inset of Figure 4.2, the viscosity of 5 wt% aqueous P85 relative to water decreases during the unimer-to-micelle transition; this implies that the decreasing free Pluronic concentration of the unimer-solvent phase has a greater impact on the observed viscosity than the increase in non-interacting micelle volume fraction which would lead to an increase in viscosity.

The 70°C data display essentially the same early-time diffusive behavior as the 60°C data. A similar high frequency collapse was also observed in Pluronic L64 aqueous solutions at constant micellar volume fraction (Chapter 3). Analogous to hard sphere dispersions, there is a region of short-time dynamics solely dictated by hydrodynamic interactions. However, at later-times the 70°C data deviates sub-diffusively from the 60°C data, indicating the development of some elasticity. SANS data suggest that the source of elasticity owes to the interaction of rod-like micelles. The morphological transformation of spherical micelles to rod-like micelles is evident from the disappearance of a correlation peak at $\sim 68.7^\circ$C and corroborated by the depolarized dynamic light scattering data of Schillén, Brown, and Johnsen.

Figure 4.3 demonstrates the effect of hydrostatic pressure on the low-concentration P85 solution dynamics. At 20°C the solution is below the unimer-to-micelle transition and exhibits a relatively small response to the applied pressure. However, at 40°C there is a more pronounced transition to lower microscopic creep values, corresponding to an increase in viscosity. The most noticeable feature is the viscoelasticity present at 70°C, which becomes only slightly discernible as the pressure is increased to 34.5 MPa. At elevated pressures the microscopic creep looses all viscoelastic character and becomes fully diffusive. These results suggest that aqueous P85 has similar structural susceptibility to hydrostatic pressure to that of F88. Furthermore, this implies a link between the hydrostatic pressure and the observed mechanical properties. Although microscopic densification of a simple fluid yields subtle configurational changes that lead to inconspicuous changes in property, the
presence of complex structures act as a medium to amplify the stimulus into a large-scale material property – as will be even more apparent at higher P85 concentrations.

Figure 4.3  The microscopic creep data for 5 wt% P85 pressure sweep at (a) 20°C, (b) 40°C, and (c) 70°C. Insets are the proportionally increased scaling of the data from $1 \times 10^{-5}$ to $2 \times 10^{-5}$ seconds.
As suggested by Mortensen et al., increasing hydrostatic pressure has the analogous effect of decreasing temperature, making H$_2$O a better solvent for Pluronics.$^1$ Thus, increasing pressure causes a shift from micelles to unimers, yielding an increase in observed viscosity.

\[
\text{Unimer} \xrightleftharpoons[^T][^P] \text{Micelle}
\]

Focusing on the sub-diffusive behavior at 70°C, Figure 4.4 highlights the diminution of elasticity by either increasing pressure or decreasing temperature. The high frequency data collapse to a single curve further supporting the idea that hydrostatic pressure affects Pluronic behavior in a similar way as temperature, controlling the solvent quality.

![Figure 4.4](image)

Figure 4.4 Effect of pressure and temperature on the dynamical behavior of 5 wt% P85 in H$_2$O.

### 4.4 The Micellar Crystalline Phase, 25 wt% P85

SANS studies reveal the presence of a paracrystalline solid at P85 concentrations greater than 20 wt% in D$_2$O.$^{3,7}$ Accounting for the higher D$_2$O density relative to H$_2$O, a higher concentration of 25 wt% was elected to ensure the disorder-to-order transition was captured.$^1$

---

$^1$ The volume equivalent weight fraction of 20 wt% P85 in D$_2$O is $\sim$22 wt% P85 in H$_2$O.
Figure 4.5  Microscopic creep for 25 wt% P85 in H_2O from 20 to 35°C (top plot) and 40 to 60°C (bottom plot).  The inset is the fit zero frequency viscosity, $\eta_0$, obtained from fitting the data from the top and bottom plots.

Figure 4.5 shows the microscopic creep response from 20 to 60°C.  There is a large shift to slower dynamics with a minimum around 35°C.  Although this temperature corresponds well with the middle of the expected paracrystalline phase given by SANS measurements in literature, we anticipate a more substantial dynamical response associated with the transition from a disordered liquid to an ordered solid.  The microscopic creep shows a diffusive escape at long-times indicative of a viscoelastic liquid for all the temperatures considered.  The major difference between the data presented here and structural studies given in the literature is the use of H_2O instead of D_2O.  In the following subsections, we examine the delicate nature of P85 solubility with regards to isotopic substitution in water.
4.4.1 The Solubility of Ethylene oxide-Based Polymers

The solubility of PEO in water is a fortuitous consequence of commensurate distances between the ether oxygens along the polymer backbone, as illustrated by the insolubility of poly(methylene oxide) and poly(trimethylene oxide) in water. Based on this observation Kjellander and Florin\textsuperscript{19} constructed a spatial model of PEO in water, demonstrating preferable alignment of PEO within observed water configurations. The structure of liquid water is observed to form short-lived ‘icebergs’ at standard temperature and pressure.\textsuperscript{20} The basic idea is that as the temperature is elevated the lifetime of these icebergs decreases to the point where the water can no longer maintain PEO in solution. Therefore this model predicts the inverse solubility of PEO as a function of temperature – that is its solubility decreases with increasing temperature. Oligomeric PPO is only soluble in water at low temperature, which is a consequence of the pendant methyl groups interfering with the water structure.

Unfortunately, the above model does not predict the well-known solubility of PEO in other polar solvents. Karlström\textsuperscript{21} found that the most polar confirmation of the -O-C-C-O- sequence within PEO is a trans-gauche-trans orientation, which is also the most probable confirmation at low temperature. At high temperatures, the probability of PEO adopting other non-polar orientations increases. This preferred polar confirmation theory explains the solubility behavior in water as well as in other polar solvents.

It is important to note that the literature tends to cite one theory and exclude the other. A simple observation is that these theories may not be mutually exclusive. It is hard to discount the effect of the local order of water on the overall solubility of a solute. The overall solubility behavior of ethylene oxide-based polymers may be a combination of the preferable polar conformation as well as the underlying solvent structure.

4.4.2 The isotopic effect: D\textsubscript{2}O versus H\textsubscript{2}O

Small atomic substitutions on the backbone of PEO have large consequences on the solubility characteristics of the system as evidenced by the lower LCST of PPO. The seemingly minor substitution of deuterium for hydrogen yields dynamical and structural effects manifested as changes in the observed bulk properties.\textsuperscript{22} Branca et al.\textsuperscript{23, 24} performed comparative studies on a 3,400 g/mol PEO standard in both D\textsubscript{2}O and H\textsubscript{2}O; their Raman scattering results indicate a higher degree of conformational order for PEO in H\textsubscript{2}O relative to PEO in D\textsubscript{2}O. Those authors concluded that since the hydrogen bonding between D\textsubscript{2}O molecules is stronger, the energy gain for PEO-D\textsubscript{2}O bonding is less, making H\textsubscript{2}O a better solvent for PEO.
The solubility behavior of the individual blocks of PEO and PPO is the source of the morphological diversity observed in Pluronic systems. While small changes in the structure of the Pluronic molecule yield large shifts in the phase behavior, there are conflicting reports in the Pluronic literature on the effect of isotopic substitution of deuterium for hydrogen in water. Goldmints et al.\textsuperscript{10} compared the static scattered light intensity of 5 wt\% P85 solutions in H\textsubscript{2}O and D\textsubscript{2}O and concluded that the effect was negligible. In contrast, Gille et al.\textsuperscript{25} examined 5 wt\% P85 solutions in both solvents using pulsed field gradient (PFG) NMR and found that the hydrodynamic radius of the micelles was significantly larger in H\textsubscript{2}O than in D\textsubscript{2}O under the same conditions. These authors proposed that hydration stabilizes the trans-gauche-trans polar confirmation of the PEO chain and that D\textsubscript{2}O promotes stronger coiling, yielding a more compact PEO corona. Meilleur et al. present further evidence for an isotopic effect using heat capacity data; they show that micellization occurs at a lower temperature for D\textsubscript{2}O than H\textsubscript{2}O.\textsuperscript{26} In other cases, the D\textsubscript{2}O effect was noted yet discounted as the critical micellization temperature was just mildly affected.\textsuperscript{1}

Figure 4.6 shows the zero frequency viscosity obtained from DWS measurements of the microscopic creep for 25 wt\% P85 solutions at five different D\textsubscript{2}O to H\textsubscript{2}O ratios. As the composition of the solvent becomes more deuterated the sample dynamics slow down, indicating increasing viscosities at a given temperature. For samples with 75 wt\% or more D\textsubscript{2}O there was a clear sol-gel transition. The phase behavior for pure D\textsubscript{2}O corresponds well with the SANS data given in reference 13.
Figure 4.6  Zero frequency viscosity, $\eta_0$, obtained with DWS for 25 wt% P85 samples in different ratios of H$_2$O and D$_2$O. Lines exiting the top of the plot indicate solid-like behavior over the time-scales considered.

Solvent deuteration affects the Pluronic phase behavior owing to stronger D$_2$O self-interaction compared to that between H$_2$O molecules; this results in a well-known higher density, but also affects the Pluronic self-association behavior since micellization occurs at lower temperatures in D$_2$O. Also, it should be noted that higher solvent-density equates to having slightly less mass-per-volume concentration in the H$_2$O-rich samples than in the D$_2$O-rich samples. While the behavior shown in Figure 4.6 is in part due to mass-per-volume concentration differences, these concentration differences alone are not sufficient to account for the absence of the disorder-to-order transition in the H$_2$O-rich samples. Thus, the stronger inter-D$_2$O associations significantly affect the phase behavior of P85. The complex behavior of P85 amplifies the subtle solvent interactions, which are manifested in the form of large length-scale phase behavior and its subsequent impact on solution dynamics.
4.4.3 Dynamical Behavior of 25 wt% P85 in D₂O at Ambient Pressure

The probe particle displacement measurements described in §4.4 exhibited significant deviations from what would be expected to occur for a disorder-to-order transition. Recognizing the isotopic effect as the source of this discrepancy, we re-evaluate the system in pure D₂O.

Figure 4.7 25 wt% P85 in D₂O at ambient pressure as a function of temperature.

Figure 4.7 shows the evolution of micellar dynamics as manifested in the microscopic creep leading to the observed zero frequency viscosity shown in Figure 4.6 and reveals three regions of differing behavior. For sufficiently low temperatures (15 and 20°C) the microscopic creep collapses to a single curve at high frequencies. As the temperature is increased the micelles become more numerous, and, therefore crowded with the microscopic creep beginning to decrease significantly thereby reflecting the increasing viscosity. At 35°C the microscopic creep exhibits a slow sub-diffusive evolution indicative of a strongly elastic gel.

SANS data reveal a correlation peak associated with micelle-micelle interactions, which strengthens with increasing temperature. The growth of the correlation peak is accompanied by a shift towards higher micellar volume fractions. Increased crowding eventually leads to a coexistence between micelles and micellar crystals; such coexistence has been confirmed experimentally with ‘model’ hard-spheres approaching the volume fraction freezing-point. The highest temperature shown in Figure
4.7 (35°C) is associated with micellar freezing, where micellar crystalline domains span the sample volume. The existence of a shear aligned BCC crystal is indicated by distinct peaks found in SANS spectra.7

4.4.4 Hydrostatic Pressure Influence on the Dynamical Behavior of 25 wt% P85 in D$_2$O

In §4.3 we examined the influence of hydrostatic pressure on the dynamical properties of aqueous 5 wt% P85 solutions as reflected by the Brownian motion of embedded probe particles. In the previous section, we considered a higher concentration solution of 25 wt% P85 in D$_2$O, thereby observing a disorder-to-order transition upon increasing temperature. The disorder-to-order transition is marked by a shift from diffusive to sub-diffusive microscopic creep (mean square displacement) scaling, which is confirmed in the literature by SANS measurements that indicate the existence of a soft micellar polycrystal. In Figure 4.8, the influence of hydrostatic pressure on the nature of these transitions is examined.

The application of hydrostatic pressure from 0 to 34 MPa at 20°C (Figure 4.8.a) results in a jump to higher microscopic creep values 

\[ i.e., \] to lower viscosities. The microscopic creep then decreases with further increases in hydrostatic pressure; this behavior is clearly demonstrated by the extracted zero frequency viscosity shown in the inset of Figure 4.8 (a). The overall trend is similar to microscopic creep measurements of 5 wt% P85 in water solutions (§4.3) upon increasing pressure, excluding the initial jump. In the 5 wt% solution case, it was explained that Pluronic molecules in the bulk had a greater influence on the observed viscosity than in the form of non-interacting micelles. However, for higher concentrations, the system is able to reach higher micellar volume fractions wherein micelles may interact \( via \) excluded volume. When inter-micellar interactions become important, the Einstein relation (see Equation (4.3)) considerably underestimates the observed viscosity. Thus, we can identify the initial jump to lower viscosities as a diminution of inter-micellar interactions owing to the decreased micellar volume fraction. In the non-interacting micelle regime, the increase in viscosity is attributed to the dissolving of the micelles into unimers, thereby enhancing the solvent viscosity.
Figure 4.8  The response of 25 wt% P85 in D₂O upon application of hydrostatic pressure for (a) 20°C, (b) 35°C, (c) 45°C, and (d) 70°C (every third datum point shown for clarity). The inset of the top figure shows the zero frequency viscosity found using the curves in (a). In the bottom three figures, the pressure decreases from left to right.
More interesting is the effect of hydrostatic pressure on the so-called soft micellar crystal (panels b and c in Figure 4.8). Beginning at pressures of 207 MPa and decreasing towards ambient, we observe a transition from a viscous sol to an elastic gel. Prior to the formation of a sample spanning micellar polycrystal, a coexistence of crystalline and isotropic regions is predicted to occur. The two microscopic creep traces at the lowest pressures in Figure 4.8 (b) and (c) are indicative of this coexistence. Further decreasing the pressure yields a flat sub-diffusive region with a relaxation, if any occurs, beyond the time-scales considered here (Note that in neither panel is ambient pressure displayed).

Although both the 35 and 45°C isotherms show similar trends transitioning into the micellar crystalline region, their high-pressure behavior shows slightly different character. At the highest pressures, the 35°C isotherm begins to show a non-interacting-to-interacting micellar transition recognized at lower concentrations and temperatures. Over the same pressure range, the 45°C isotherm is still within the interacting micellar regime – as indicated by the strong pressure dependence of the microscopic creep and therefore the viscosity. This indicates that at lower temperatures the conversion of unimers to micelles upon decreasing pressure occurs more readily. A similar finding has been recognized in the Pluronic F88 system.

Structural studies at ambient pressure indicate a transition from a micellar crystal to compact rods at higher temperatures. The 70°C isotherm shown in Figure 4.8 (d) has a significantly different sol-to-gel transition than that observed for the 35 and 45°C isotherms. First the sol-to-gel transition occurs over a much larger range of pressure, from 69 MPa to ambient. This is consistent with the picture of micellar growth leading to longer-relaxation time. Second, the developing plateau modulus is at least an order of magnitude larger for the high temperature gel compared to the low temperature solid. Furthermore, it appears that the developing plateau modulus is less flat (i.e., larger slope) for the higher temperature solid. Last, there is a distinct transition between high and low pressures at high frequencies (i.e., short-times).

At high frequencies the microscopic creep for the 70°C isotherm shows a transition between two limiting behaviors. The high-pressure high frequency limit shows similar behavior to that found at lower concentrations, reflecting a region of similar hydrodynamics. The low-pressure high frequency limit is attributed to entanglement of elongated micelles, transitioning to the worm-like micellar limit.

---

† Here I refer to the creep plateau modulus, \( J_p \). The stress relaxation plateau modulus, \( G_p \), is approximately inversely related to the creep plateau modulus (\( J_p \sim 1/G_p \)), thus \( G_p(T=45°C) \sim 10 \cdot G_p(T=70°C) \).
The micelles are essentially trapped in a mesh that displays similar hydrodynamics once the micellar entanglement size is reached.

### 4.4.5 The Dynamical Phase Diagram of 25 wt% P85 in D₂O

With the collection of microscopic creep traces over a vast range of temperature and pressure, one can construct a phase diagram based on dynamics. In order to obtain a proper 3-dimensional representation, each microscopic creep must be reduced to a single parameter representing the same characteristic of that curve. Although somewhat arbitrary, we select the criterion of a viscous and elastic modulus crossover point as marking the transition to a solid-like phase (for more information see Chapter 3). This inherently restricts this analysis to the time-scale set by the diffusing wave spectrometer. However, as argued in Chapter 3, this is an appropriate time-scale to explore the Pluronic micellar formation of large length-scale structures.

![Phase Diagram](image)

**Figure 4.9** T/P phase diagram for 25 wt% P85 in D₂O. 

- Indicates micellar crystalline solid, and 
- indicates entangled cylindrical micelles.

The phase diagram given in Figure 4.9 is consistent with ambient pressure structural measurements that demonstrate the presence of two solid-like regions: (i) the low temperature solid corresponding to micellar crystalline structure and (ii) the high temperature solid corresponding to entangled rod-like (or worm-like) micelles. Application of pressure effectively melts each solid at a given temperature, ultimately yielding a liquid-like sol. That is, at high pressures all of the microscopic creep curves display a diffusive escape, allowing for the determination of the zero frequency viscosity.
Figure 4.10 shows the zero frequency viscosity found along the 207 MPa isobar, revealing a transition from non-interacting to interacting micelles, with an apex of interacting micelles occurring at \( \sim 55^\circ C \). The apex of micellar interactions at ambient pressure results in the formation of a micellar crystalline phase (Figure 4.9). Thus, the location of this apex shifts to higher temperatures upon increasing hydrostatic pressure. Increasing hydrostatic pressure shifts the unimer-micelle equilibrium towards more unimers, which is effectively countered by increasing the temperature. Ultimately, this relationship establishes a ‘temperature-pressure correspondence’ recognized in other Pluronic systems.  

### 4.5 The Micellar Crystalline Phase – Take II, 35 wt% P85

At higher P85 concentrations, ambient pressure structural studies reveal a micellar crystalline phase extending to lower temperatures. Colloidal sphere thermal motion measurements confirm similar transitions found in 25 wt% P85 in D\(_2\)O solutions of §4.4.3. Three select isotherms for a 35 wt% P85 in H\(_2\)O solution are shown in Figure 4.11, which are qualitatively similar to those found for 25 wt% P85 in D\(_2\)O solutions (see Figure 4.8). The primary difference is that, for the higher concentration, the solid phases extend to far greater pressures before undergoing a gel-to-sol transition.
Figure 4.11  Microscopic creep pressure sweeps along the (a) 20°C, (b) 58°C, and (c) 68°C isotherms (every third point shown for clarity). The inset of (a) is the zero frequency viscosity, \( \eta_0 \), found by fitting the 20°C isotherm data from 0 to 207 MPa.
In Figure 4.11 (a) the 20°C isotherm, the microscopic creep shifts to higher values upon increasing hydrostatic pressure; this viscosity decrease is associated with the decreasing micellar volume fraction. The transition from increasing to decreasing microscopic creep values at 68 MPa is correlated with the transition from interacting to non-interacting micelles. Microscopic creep values at higher pressures (not shown) display a gradual decrease to lower values. The inset shows the zero frequency viscosity up to 207 MPa, clearly showing the transition from a unimer-solvent dominated viscosity to that of interacting micelles.

The sol-to-gel transition occurs at much higher pressure and temperature than that found for 25 wt% P85 in D₂O solutions (see phase diagram in Figure 4.9). The 58°C isotherm for 35 wt% P85 in H₂O shows a sharper sol-to-gel transition than the one observed for the less concentrated samples. However, the general isothermal qualitative microscopic creep behavior during the transition is essentially unchanged, indicating a similar coexistence of micellar liquid and crystalline domains. Once the micelle volume fraction reaches the freezing volume fraction, φₚ, the micelles coexist with the micellar crystalline domains. Upon further decreasing the pressure, or likewise increasing the micellar volume fraction, the melting volume fraction, φₘ, is reached and the system becomes crystalline. SANS data reveal that aqueous P85 undergoes crystallization at φₘ ∼ 0.53, which is in agreement with hard sphere simulations of φₘ = 0.545.7, 13, 28

The 68°C isotherm (Figure 4.11 (c)) exhibits qualitatively similar microscopic creep behavior as the 70°C isotherm for 25 wt% P85 in D₂O solution (see Figure 4.8 (d)). However, the sol-to-gel transition is significantly shifted to higher pressures, and the ambient pressure microscopic creep does not completely relax at the time-scales considered here. Additionally, only a low-pressure high frequency collapse is observed, whereas both a low- and a high-pressure high frequency limit was observed for the 25 wt% P85 in D₂O solution. It is most likely that the high-pressure limit for the 35 wt% in H₂O solution is shifted to higher pressures than considered in this study (i.e., beyond 207 MPa).

4.5.1 Transitions into the Micellar Crystal 35 wt% P85 in H₂O

The exploration of the 35 wt% P85 in H₂O solution over temperature and pressure phase space can be summarized by extracting the zero frequency viscosity from DWS colloidal sphere thermal motion measurements as shown in Figure 4.12. Furthermore, we mark the location of the so-called disorder-to-order transition, i.e., the melting pressure by dashed vertical lines. In the limit of high pressures, the zero frequency viscosity exhibits a linear increase with increasing pressure; this is associated with a shift from micelles to unimers, where the unimer-solvent contribution dominates the observed viscosity. For each temperature, the zero frequency viscosity exhibits a pressure minimum associated
with the transition from non-interacting to interacting micelles. As the pressure is further decreased, there is a shift from unimers to micelles resulting in a pronounced increase in the observed viscosity.

Figure 4.12  Zero frequency viscosity, \( \eta_0 \), obtained using DWS. The vertical dashed lines indicates the divergence of the viscosity marked by the presence of sub-diffusive scaling at the latest times considered.

In Figure 4.13, the melting pressure is subtracted from the abscissa in Figure 4.12, emphasizing the discontinuity in the viscosity at the freezing pressure. The different symbols also highlight differing behavior in the region of interacting micelles between low and high temperatures. It is possible that the higher temperature deviation could be due to the micelles becoming ellipsoidal in shape.
Figure 4.13 Zero frequency viscosity, $\eta_0$, obtained using DWS, versus the pressure minus the pressure at which the Pluronics become crystalline, $P_c$. The different symbols and lines are used to highlight differing behavior.

4.5.2 Light Transmission and 90° Static Light Scattering Measurements at Ambient Pressure

For a range of temperatures above 50°C at ambient pressure, the transmission of light through the sample becomes more diffuse but still translucent in appearance, reminiscent of shaved glass in water. Above approximately 60°C, the sample returns to its previously limpid state. The temperature range of 50°C to 60°C roughly corresponds to the transition between the micellar crystalline and the rod-like micellar phases. Glatter et al. made similar observations using light transmission measurements, reporting a large drop in intensity during this transition.\textsuperscript{29} Using SANS, Mortensen speculated the formation of a micro-emulsion, noting that the structure factor was similar in character to an $L_\alpha$-phase of a low-molecular weight surfactant aqueous solution.\textsuperscript{7}

Light transmission and 90° static light scattering measurements were performed over a wide range of temperatures at ambient pressure. Light transmission measurements were carried out by directing a 5 mW He-Ne Laser ($\lambda = 632$ nm) through a sample of fixed path-length ($\sim 4.5$ mm) and monitoring the transmitted intensity, which was subsequently normalized by the transmission intensity of air.
90\degree static light scattering measurements were conducted following a procedure similar to that described in Chapter 3 (§3.2.2). In this procedure, the excess Rayleigh ratio at 90\degree was converted to the inverse osmotic compressibility by assuming a relatively angle independent scattering profile (i.e., the 90\degree scattering is essentially the same as the zero angle scattering). This assumption was justified by examining the scattered intensity from angles of 45\degree to 135\degree, which relates to a scattering vector range of $4.8 \times 10^{-4}$ to $2.3 \times 10^{-3}$ Å$^{-1}$. The excess Rayleigh ratio at 90\degree is related to the inverse osmotic compressibility as:

$$
\left( \frac{\partial \pi}{\partial c} \right)_{T,P} = \frac{K_c}{R_\theta} \left. \right|_{\theta \to 0} RT \approx \frac{K_c}{R_\theta} \left. \right|_{\theta = 90^\circ} RT \quad (4.4)
$$

where $R_\theta$ denotes the Rayleigh ratio, $\pi$ is the solution osmotic pressure, $c$ is the solution concentration, and $K$ is an optical constant. As noted in Chapter 3 (§3.2.2), Pluronic samples as received are not “dust free”; as such one should avoid interpreting the absolute magnitude, but rather consider differences upon changing temperature.

Figure 4.14 shows the normalized transmission (top plot) and the 90\degree static light scattering data (bottom plot) over a range of temperatures at ambient pressure. The normalized transmission has a relatively flat profile for temperatures less than 50°C. In the temperature range of 50 to 60°C the transmitted intensity drops several orders of magnitude, which we shall denote as the crystal-to-rod transition. At 60°C there is an increase in transmission, this roughly corresponds to the rod-like micellar region. At \sim 81°C there is a drop in transmitted intensity, which could be easily mistaken as an outlier; however as we find in the next section, this is most likely associated with a transition into a yet unidentified high temperature phase. Between 81°C and the phase separation temperature of \sim 86°C, the measured transmitted intensity returns to a similar value as found at low temperatures. Using SANS, Mortensen finds the return of a correlation peak, which he attributes to the presence of a liquid-like high temperature micellar phase.\footnote{Using SANS, Mortensen finds the return of a correlation peak, which he attributes to the presence of a liquid-like high temperature micellar phase.}

The estimated inverse osmotic compressibility is shown in Figure 4.14 (bottom plot) and corresponds well to the aforementioned transmission measurements. Most notable is the drop in intensity from 50 to 60°C, showing a corresponding large increase in 90\degree scattering, which saturates the detector (note that $\partial \pi / \partial c \sim 1/L_{w0}$). The image shown in the bottom plot of Figure 4.14 is the scattering pattern from a 35 wt\% P85 sample in a 2 mm cell, exhibiting a diffuse ring and confirming the presence of large length-scale structures. Clearly, the approximation made in Equation (4.4) is no longer valid since the intensity at the 90\degree detector is a poor approximation to the zero angle scattered intensity. The scattering pattern in this micelle-to-rod transition is attributed to a coexistence between regions of spherical and cylindrical micelles. Such coexistence has been found in other triblock surfactants.
such as the coexistence of spherical and threadlike micelles in a 6000 molecular weight PEO-PIB-PEO triblock surfactant confirmed using TEM.\textsuperscript{31}

At lower temperatures, the rise in inverse osmotic compressibility, showing a maximum at 25°C, is related to the formation of a stiff paracrystalline gel. For temperatures above 35°C, there is a gradual drop in the inverse osmotic compressibility, indicating larger micellar fluctuations. This drop continues onto 75°C, the highest temperature considered.

Figure 4.14 The normalized transmitted intensity (top plot) and the estimated inverse osmotic compressibility (bottom plot) for 35wt% P85 in H\textsubscript{2}O. The approximate inverse osmotic compressibility is based on the 90° detector (q \(\cong\) 1.7\(\times\)10\(^{-3}\) Å\(^{-1}\)). Empty circles indicate saturation of the 90° detector due to large length-scale scattering. In this region, the sample appears hazy and produces a diffuse ring pattern (image: 632-nm laser light scattering through a 2 mm sample at 55°C).
4.5.3 High Pressure Dynamical Phase Diagram of 35 wt% P85 in H$_2$O

Based solely on ambient pressure transmission and 90° light scattering measurements, one might interpret the 58°C isotherm observed in DWS colloidal sphere thermal motion measurements (§4.5) as the transition into a rod-like micellar phase. However, the qualitative behavior of the microscopic creep during this transition (Figure 4.11.b) indicates the existence of a micellar crystalline phase up to 58°C. To unravel this apparent inconsistency, we explore the total phase space from 15 to 85°C and 0 to 225 MPa, making both intensity and dynamic measurements. Thus, we can construct a dynamical phase diagram as similarly done in for the 25wt% P85 in D$_2$O sample (§4.4.5) with the addition of high-pressure transmission intensity information.

The phase behavior shown in Figure 4.15 is more pronounced than the phase diagram obtained for the 25 wt% P85 in D$_2$O solution, marked by the persistence of solid domains to much higher pressures. Included is a low transmission intensity band (cyan horizontal lines), which encircles the rod-like micellar region. The dashed boundary filled by (red) downward diagonal lines indicates an extended rod-like elastic solid; in this region, the microscopic creep trace shows gradual relaxation but still has a liquid-like to solid-like crossover of the viscous and elastic modulus. In the region of (red) crossed lines, the intensity measurements show a sharp increase, and dynamics measurements reveal very little relaxation over the time-scales considered (< 0.1 second).

---

§ Approximately 510 and 370 unique phase points were evaluated using intensity transmission and DWS, respectively.
In Figure 4.15 we notice the union of a low transmission region and the micellar crystalline region. As the temperature is increased, the micelles begin to grow, while still maintaining a solid-like elastic state. Eventually, the spherical and rod-like micellar coexistence destroys the crystalline order, and the system transitions into a liquid-like state. Further increasing temperature leads to further micellar growth; these micelles become entangled and the system transitions into an elastic solid-like phase.

4.5.4 High Temperature Isotherm

In Figure 4.16 the 83°C microscopic creep isotherm indicates a reversal of the dynamical behavior. Starting at 207 MPa and upon decreasing pressure a distinct modulus evolves. Further decreasing the pressure results in dynamical reversal, where the microscopic creep traces shift towards higher values with a concomitant loss of the distinct modulus. Interestingly, one can find nearly indistinguishable microscopic creep traces at two separate pressures along the 83°C isotherm (e.g., 35 & 70 MPa, 6.9 & 141 MPa, and 0 & 145 MPa). This behavior indicates that at high temperatures the micelles revert to a non-entangled state before phase separation occurs. This is consistent with Mortensen’s SANS data showing the return to an isotropic liquid with a micelle-micelle correlation.
peak. However, to our knowledge, the existence of such a high temperature micellar phase has not been committed to phase diagrams within the voluminous Pluronic literature database.

Figure 4.16 83°C isotherm for 35 wt% P85 in H₂O (every third point shown for clarity). The top plot shows the isotherm from 207 to 70 MPa and the bottom plot shows 35 to 0 MPa.

It is curious that the Pluronic micelles would undergo a thermodynamically favored rod-like growth upon increasing temperature and then revert to shorter micelles at still higher temperatures. One may speculate that entangled cylindrical micelles suppress large length scale concentration fluctuations, leading to phase separation. That is, the breakup of long cylinders into smaller micelles provides a mechanistic route that allows for large concentration fluctuations, as required for phase separation. Mortensen’s SANS data and the elasticity found in our measurements suggest increased inter-micellar interactions similar to those found in the L64 system directly before phase separation (Chapter 3).
4.6 Summary and Conclusion

DWS colloidal sphere thermal motion studies allow for the exploration of high frequency dynamical information over a wide range of temperature and pressure. In these studies, we have employed a high-pressure scattering cell to examine the phase space of aqueous Pluronic P85 solutions. For low concentrations, we have detected the presence of non-interacting micelles, which elongate at high temperatures and interact to yield subtle elasticity. At higher concentrations, micelles interact and self-organize, producing characteristic transitions into either a micellar crystal at moderate temperatures or entangled cylindrical micelles at high temperatures.

Throughout the aqueous Pluronic P85 phase space, the unimer-micelle equilibrium plays a significant role in the observed dynamics. Favorable solvent conditions shift the equilibrium towards Pluronic unimers. For low concentrations, the enrichment of the solvent with unimers increases the observed viscosity; i.e., Pluronic in the unimer-solvent phase has a greater impact on the observed viscosity than in the form of a non-interacting micelle. Increasing solvent quality by either decreasing temperature or increasing hydrostatic pressure results in a larger viscosity. However at larger Pluronic concentrations, micelles are no longer dilute and are able to interact by simple excluded volume, significantly enhancing the viscosity. The expected transition from non-interacting to interacting micelles was observed for a 25 wt% P85 in H₂O solution, indicated by a minimum in the viscosity upon changing temperature or hydrostatic pressure.

While exploring the dynamical landscape of a 25 wt% P85 in H₂O solution, there was an unexpected absence of a micellar crystalline region at higher temperatures, which had been previously noted in SANS studies.¹³ We found that isotopic substitution of deuterium for hydrogen in water yields a markedly different phase diagram; this is partly owing to fact that H₂O is a slightly better solvent for Pluronics than D₂O. Exploration of P85 aqueous solution phase behavior using D₂O reveals the presence of a characteristic sol-to-gel transition, corresponding well to previous SANS measurements.

The microscopic creep traces obtained by changing the hydrostatic pressure for a given isotherm yield characteristic microscopic creep transitional ‘fingerprints’, allowing for the construction of a dynamical phase diagram. For a 35 wt% P85 sample in H₂O solution, we find both a moderate and a high temperature solid-like region, recognized as a micellar paracrystalline phase and an entangled rod-like phase, respectively. High-pressure intensity transmission measurements reveal a low intensity band encircling the entangled rod-like region. We hypothesize that this region is due to the coexistence of regions rich in spherical and rod-like micelles, as similarly found in other aqueous triblock surfactants.³¹ At the highest temperatures considered (85°C), a breakdown of the cylinders
into smaller micellar bodies occurs, which is corroborated by older SANS data. The presence of this phase is rather unexpected; it is speculated to be associated with the development of phase separation at higher temperatures.

Complex fluids tend to amplify subtle microscopic interactions resulting in gross changes of observable macroscopic behavior. We have demonstrated that subtle changes in water by densification using hydrostatic pressure, by increasing thermal energy, or even by isotopic substitution lead to discernable large-scale effects in aqueous Pluronic solutions. More generally, we have demonstrated the utility of DWS tracer studies to explore complex fluids in high pressure and temperature environments, allowing for the construction of phase diagrams based on dynamical pathways.
References


