Using Coherent Small Angle Xray Scattering to Measure Velocity Fields and Random Motion

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ABSTRACT

The dynamics of cross-linked polymers under stress, such as those that make up rubber, are still not well understood. A combination of coherent xray homodyne and heterodyne techniques is used in order to measure fluctuations of the system when stretched. The combination of both techniques allows for the measurement of flow patterns, as well as the random nature of the system. After data analysis, the results show that the measurements successfully captured this flow information. The flow velocity was discovered to have a time-dependent nature similar to that of the stress-strain curve. After the flow velocity was extracted, the random nature of the system was analysed. This random motion was discovered not to be dominated by conventional diffusion, but some slower random process.

ABRÉGÉ

La dynamique de polymères réticulés de stress, telles que celle qui compose le caoutchouc, n'est pas encore bien comprise. Une combinaison de techniques homodynes et hétérodynes de rayons x coherentes est utilisé pour mesurer les fluctuations du système, une fois étiré. La combinaison des deux techniques permet la mesure des régimes d'écoulement, ainsi que le caractère aléatoire du système. Après l'analyse des données, les résultats montrent que les mesures ont réussi à capturer cet information. La vitesse d'écoulement a été découverte de contenir une nature en fonction du temps semblable à celle de la courbe contrainte-déformation. Après la vitesse d'écoulement a été extraite, la nature aléatoire du système a été analysé. Ce movement a été découvert de ne pas être dominé par la diffusion classique, mais de certains processus aléatoires plus lents.

DEDICATION

To my parents, Corinne and Roger Lhermitte

To my brother, Charles Lhermitte

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When I first came to McGill, I had very little knowledge about the field of Xray Intensity Fluctuation Spectroscopy. All I knew was that I enjoyed physics and using the power of computer science to further this pleasure. I also found Montreal to be a wonderful city to spend my time engaging in such studies. I had visited it before and really enjoyed the atmosphere, the "non-Miami" weather, and the francophone culture. When I met Prof. Mark Sutton for the first time, I found his enthusiasm about physics as adaptiveness to new technologies to fuel it further uncanny. I believe when pursuing higher education that there is nothing more paramount for it than motivation and enthusiasm. Otherwise, the long journey is not worth it. This is what he showed me and enabled me to discover. I would like to thank Prof. Mark Sutton for sharing his enthusiasm with me as well as enabling me to achieve the satisfaction of answering still unknown questions by working on current problems in physics. I would also like to thank him for his incredible flexibility and openness. Without this, I would not have felt relaxed enough to discover what I really do enjoy and why I'm here. I also would have never been able to explore the many non-conventional open source technologies that exist there to aid us in our data analysis. I believe the necessity to use Linux and the use of open source programs with perhaps a bit steeper learning curves have enabled me to obtain a deeper understanding of concepts and ideas crucial to the research.

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CHAPTER 1 Introduction

1.1 Motivation

Xrays were discovered by W.C. Röntgen in 1895. Ever since their discovery, they have been used for many applications, such as to probe the atomic structure of matter. Some of the earliest applications included measuring crystal structures and the positions of atoms. As brighter and brighter xray sources are being developed, such as synchrotron radiation sources, applications are steadily increasing. One example is the ability to measure ferromagnetic magnetization density from a weak magnetic coupling between xrays and ferromagnetic samples [1]. The increase of computational power and storage has also enabled more interesting analysis of scattering by xrays. An example of this is the newer generation CAT scans that analyze scattering from xray images above and below the K-absorption threshold of iodine injected into a patient prior to the measurement [2].

With the advent of undulators in third generation synchrotron sources, xray beams have become more coherent. This has opened a new branch of experiments taking advantage of this coherence under the name of xray intensity fluctuation spectroscopy (XIFS) measurements. Just as a hologram uses the coherence of visible light to add depth to an image, XIFS measurements can use this coherence to gain previously inaccessible information about the fluctuations of a sample. An example of this is using XIFS to measure the dynamics of block copolymer micelles [3].

However, due to the nature of the experiments, using these more coherent sources to make interesting measurements also requires creativity and innovation as well as computational and technical skills. An example of this is a technique called heterodyning. Heterodyning is a technique where a reference beam is introduced to interfere with the scattered beam in a sample. The successful application of this technique allows the measurement of the flow of colloids[4].

An interesting application of this technique is to study cross-linked polymers. Cross-linked polymers are long chains of molecules interconnected to each other at a certain number of sites. They make up a wide range of materials such as those used in plastic packaging and rubber tires. The reaction of these polymers under stresses and strains is still not well understood, nor do we have a theory to describe them. New experimental measurements would help us to better understand how these materials work.

I discuss in this thesis the analysis of heterodyne XIFS measurements on a carbon black cross-linked ethylene-propylene polymer, a type of rubber. The rubber is stretched, and the sample is measured by homodyne and heterodyne XIFS alternatively, for over an hour. This is repeated for several stretches. Homodyne measurements were done to complement the heterodyne data. Their analysis is also discussed in this thesis.

2



Figure 1–1: Coordinate system of the experimental setup. The gray sphere is a sphere of radius q. The independent coordinates q, θ' and ϕ are the polar coordinates of the system with the base of the \vec{q} vector being the center. These are the conventional xray scattering coordinates with the angle 2θ representing the physical location of the detector (or a pixel of it).

1.2 Speckle

To understand the XIFS measurements, one must first understand an important concept called speckle. A speckle pattern is an interference pattern produced by the radiation emanating from different sources all coherent with one another. The best way to visualize it is to start looking at the experimental data.

Imagine the usual xray scattering experiment. An incoming beam scatters off a sample into multiple directions. A CCD camera measures the intensity for different \vec{q} as can be seen in figure 1–1.

A sample speckle pattern from the measurements carried out here can be seen in figure 1–2. The black box is the shadow of the beam stop. The speckle can be seen at small angles near the beam stop. Because the sample is fluctuating, this interference pattern changes with time. One can see an example of the speckle pattern for the same measurement observed at a portion of the CCD camera for



Figure 1–2: Sample speckle pattern from the measurements. The black box at the upper right corner represents the shadow of the beam stop.

different times in figure 1–3. It is clearly seen that the speckle pattern is changing. By measuring this change, one can actually determine small movements of the particles, which cannot be done using incoherent radiation. If one averages the speckle pattern in time, one would see a smooth image. This is what conventional xray diffraction would measure. One can see such a comparison in figure 1–4.

1.3 Coherence

One learns from high school physics courses that light is a wave. Yet, if light is a wave, one should expect interference effects. Why is it then that we rarely see interference patterns from, let's say, your conventional street lights? The answer to this question, of course, is that every day light sources are not coherent. What then is coherence?



Figure 1–3: Here is a sample of a portion of the speckle pattern of homodyne data zoomed in time. Moving clockwise from the top left, each intensity image was taken 250s after the one before, consecutively. Black indicates that the pixel was not selected. The units are in ADUs, which is related to the photon count.



Figure 1–4: Comparison of an image of a speckle pattern from homodyne data with its average image averaged over 750s. Although there still appear to be some speckle due to the finite time average, the features are greatly reduced. The intensity is again measured in ADUs.

Before any definitions are made, the concept of coherence must be well understood, as the rest of the thesis will depend on this understanding. Therefore the goal of the following explanation is to give the reader an idea as to what exactly coherence is, without all the mathematical rigor (which will come later). Consider the usual Young's two-slit experiment in figure 1–5.

The interference pattern recovered will be the intensity (which is the timeaverage of the Poynting vector)[5]:

$$I = \langle S \rangle = \epsilon_0 c \frac{1}{2} \langle |\vec{E}|^2 \rangle = \frac{1}{2} \epsilon_0 c \left(\langle |\vec{E}_A|^2 \rangle + \langle |\vec{E}_B|^2 \rangle + 2 \langle \vec{E}_A \cdot \vec{E}_B \rangle \right)$$

$$= \frac{1}{2} \epsilon_0 c \left(|E_A|^2 + |E_B|^2 + 2|E_A||E_B| \langle \cos \delta_{AB} \rangle \right)$$
(1.1)
$$= \frac{1}{2} \epsilon_0 c \left(|E_A|^2 + |E_B|^2 + 2|E_A||E_B| \cos \delta_{AB} \right).$$
(1.2)



Figure 1–5: Young's Two Slit Experiment. A sample interference pattern from a two-slit experiment. The oscillations depend on the phase difference between the incoming waves. Constants chosen were arbitrary.

This formula can be broken down into two important quantities. The first two terms are the intensity of each beam, and the second term is an interference term. The interference term can be anywhere in between $\pm 2|E_A||E_B|$ depending on what the phase difference between the two points, δ_{AB} is. Saying that the two-slits are illuminated by a coherent source is just another way of saying that knowing the distance between the slits one can determine what this phase δ_{AB} will be. This phase δ_{AB} will then just depend on the difference in path lengths from points A and B to point P.

1.3.1 Spatial Coherence

Realistically, a source is generally not point sized in nature but finite in size. By the Huygens-Fresnel principle, the source may be viewed as an infinite number



Figure 1–6: Depiction of spatial coherence

of infinitesimal point sources along the wave front¹ [7]. Each point source will emit radiation spherically.

Such a source is drawn in figure 1–6. The waves from the top and bottom contributions are represented by their wavefronts. Now imagine at the point P the two waves are in phase. Moving along the wave front of contribution from point source A, it is clear that the wave fronts no longer coincide. This same idea is applied to all the intermediate points. It can be deduced that these points being closer to A will have wavefronts that go out of phase at a larger distance.

This is quantified by defining a transverse coherence length L_T . This quantity is characterized by the length at which the wave fronts between the furthest two points of the slit (A and B) are out of phase. As soon as this distance is reached, the subsequent intermediate points will also begin to go out of phase. Thus any

¹ The concept of infinite is not completely true, for an infinite number of radiating point sources produces no radiation. This is known as the evanescent wave phenomenon. Analysis of this can be found in reference [6], pages 50 and 51.

interference effects wash out beyond this point. Then $2L_T$ characterizes the length over which the wave fronts from points A and B stay in phase. From geometry, $2L_T\Delta\theta = \lambda$, which is one wave length. Since $\Delta\theta \approx \frac{a}{D}$, then:

$$L_T = \frac{\lambda}{2} \frac{D}{a}.\tag{1.3}$$

This is the definition of a transverse coherence length. Any measurement involving samples with dimensions smaller than this coherence length will be said to undergo coherent scattering. A measurement involving samples a few coherence lengths long will be said to undergo partially coherent scattering.

Thus the longer D and the smaller the source, the longer the coherence length L_T . Generally, in experiments, spatial coherence is obtained by simply placing the sample at a far enough distance. If the source is intense enough, then the intensity drop by this extra distance should not matter. This is generally not the case from chaotic sources, which emit radiation with a large angle spread. However, this is the case for xray synchrotrons, including the one at Argonne used for this experiment, thanks to the help of undulators[8]. Another interesting thing to note is that at smaller wavelengths (so higher energies), long coherence lengths are harder to obtain.

1.3.2 Longitudinal Coherence

Transverse spatial coherence is not the only type of coherence for a beam. If the beam is not monochromatic, it can be imagined to be a superposition of waves with frequencies characterized by a central frequency ω_0 and a width $\Delta \omega$. Since these waves are not of the same wavelength, they will interfere constructively



Figure 1–7: Example of temporal (longitudinal) coherence.

and destructively at different points. Imagine the wave fronts of the wave with the longest and shortest wavelengths $\lambda \pm \frac{\Delta \lambda}{2}$, as in figure 1–7. The longitudinal coherence length is defined to be the length at which these waves completely cancel one another (are out of phase). After this point, waves with intermediate frequencies will also begin to cancel one another. So $2L_L$ characterizes the distance waves can be considered in phase. From this, L_L can be easily calculated. This length is when:

$$(N+1)(\lambda - \frac{\Delta\lambda}{2}) = N(\lambda + \frac{\Delta\lambda}{2}).$$
(1.4)

This means that $N = \frac{\lambda}{\Delta\lambda} - \frac{1}{2} \approx \frac{\lambda}{\Delta\lambda}$, provided that $\frac{\Delta\lambda}{\lambda} << 1$. The longitudinal coherence length is then just:

$$2L_L = N(\lambda + \frac{\Delta\lambda}{2}) = \frac{\lambda^2}{\Delta\lambda} + \lambda \approx \frac{\lambda^2}{\Delta\lambda},$$
(1.5)

assuming that the spread in wavelengths $\Delta \lambda$ is very small. Thus the longitudinal coherence length is related to $L_L = \frac{1}{2} \frac{\lambda^2}{\Delta \lambda}$.

Generally, longitudinal coherence is obtained by the use of a monochromator, which filters the spectrum. A Germanium monochromator crystal is used in these experiments for such purposes [9].

1.3.3 Temporal Coherence

Another way to describe longitudinal coherence is in terms of the time T_c it takes for the source to traverse the distance L_L , or $T_c = \frac{L_L}{c}$. In the measurements, T_c needs to be much smaller than the correlation times of the sample. This will be explained later, but arises from the idea that the fluctuations of the beam need to be independent of those of the sample.

1.3.4 Partial Coherence

If a beam is coherent, then it will create an interference pattern dependent on the positions of the scatterers. To see things in a simpler perspective, the two-slit thought experiment is re-examined. Using

$$I_{avg} = \frac{1}{2} \epsilon_0 c \left(\langle |E_A|^2 \rangle + \langle |E_B|^2 \rangle \right)$$
(1.6)

$$\delta I = \epsilon_0 c |E_A| |E_B| \cos(\delta_{AB}), \qquad (1.7)$$

equation 1.1 simplifies to:

$$\langle I \rangle = I_{avg} + \delta I. \tag{1.8}$$

 I_{avg} is the average intensity of the source if the phase difference δ_{AB} was completely random. δI is the interference term.

First it is assumed that the two slits are the same size, and close enough together such that the scattered electric field $|E_A| = |E_B|$. It follows that δI varies between $\pm I_{avg}$. This in turn means that the intensity ranges from 0 to twice the average intensity.

Now imagine a beam is not completely coherent, but partially coherent. This is another way of saying that δ_{AB} is not completely determined, and has a small spread that must averaged over. The effect of this is to reduce the δI term. Let us name this reduction term $\sqrt{\beta}$, for notation purposes (chapter 3 of reference [10]). In this case, it is related to

$$\sqrt{\beta} = \frac{1}{\cos \delta_{AB}} \frac{1}{N} \sum_{i=1}^{N} \cos \delta_i, \qquad (1.9)$$

where the sum is on a range of random phases δ_i . As N gets large enough, β approaches zero, and the interference term dies off. Thus, for a partially coherent beam, the intensity is approximated to be:

$$\langle I \rangle = I_{avg} + \sqrt{\beta} \delta I. \tag{1.10}$$

It turns out that the general result for an arbitrary sample considered here, follows the same idea with appropriate approximations (chapter 3 of reference [10]).

1.4 Heterodyning

An interference pattern resulting from the scattering of multiple sources only depends on the relative path differences between the sources. As a result of this, it turns out that a mass movement of all the sources does not change the interference pattern. A good example of this is the fact that the Bragg peaks of a crystal do not change under a translation. This is rather troublesome for measuring flow velocities.



Figure 1–8: Example of how heterodyning works. Imagine three sources all moving the same speed initially at some initial time (red) and some final time (black). The interference pattern left will not change as the sources move, as the relative difference in phase between them remains constant. Now imagine that the bottom source stays still. The interference pattern will change now. Heterodyning involves adding some new "stationary source".

So how can flow be measured? There actually is a way around this. Basically, it is known that in order to measure any movement, it must be relative to another element in the scattering volume. Another way to think of this is in terms of the usual two slit experiment. Imagine two slits moving together. The interference pattern between them does not change. Now imagine a third slit is added that does not move relative to the laboratory frame, and keep the two moving slits. The interference pattern should now be changing, and it will be related to the relative movement between the two slits and the laboratory frame slit. A visualization of this idea is provided in figure 1–8. The "slits" are replaced with point sources for simplicity.

This technique is called heterodyning. Instead of slits, a reference sample is used. It is also required that the radiation scattered from the reference be comparable in amplitude to the radiation scattered from the sample measured. This reference sample does not move with respect to the laboratory frame, and for intents and purposes is randomly configured. The theory behind this will be discussed further in the next chapter. Conversely, the absence of such a reference sample is referred to as homodyning. The previously shown speckle from figure 1–4 is a result of a homodyning experiment.

1.5 Elastomers

The samples used belong to a wide classification of matter called elastomers. Therefore it is important to describe what exactly an elastomer is. An elastomer is a loose term for any synthetic material whose mechanical properties are similar to natural rubber. Natural rubber is typically known for its highly non-linear stress-strain curve (i.e. it does not obey Hooke's Law)[11].

Now how is an elastomer typically formed? It is usually a network of crosslinked polymers with filler particles mixed within this network. A polymer is a long chain of molecules. Polymers that are cross-linked are polymers that are linked to each other at random sites along their chain. The cross-linking of the polymers are what give it it's "rubber-like" behaviour. A filler particle is just an atom or molecule bound to certain sites in a polymer. The filler particles add rigidity by making it more difficult to strain the rubber. The reader is referred to reference [11] for more information on rubber and elasticity.

CHAPTER 2 Theory and Experiment

The measurements of the rubber system are done by XIFS. In order to understand the results of the experiment, it is important to fully understand what the measurements mean. More specifically, what is measured is the intensity of xrays scattered at different angles defined by the vector \vec{q} and at different times. To understand this, it is important to know how the dynamics of the sample relates to the intensity measured by the detector. This will require an understanding of how xrays scatter as well as the role the coherence of the beam plays. This chapter aims for two goals. One is to fully derive and explain the intensity-intensity correlation function, a result of the measurement. The other is to explain how the dynamics of the system link to the intensity-intensity correlation function measurements.

2.1 Coherent Xray Scattering

The general scattering setup is shown in figure 2–1, where $|\vec{k}_{in}| = |\vec{k}_{out}|$. This figure is the same as figure 1–1 and has been reproduced here for ease of viewing. What is actually measured in the CCD camera is an intensity. Thus a theory relating the scattering of the incoming radiation in terms of an intensity is needed. The intensity, again is the time-average of the Poynting vector. For xrays in air, this gives:

$$I = \langle S \rangle = \epsilon_0 c \langle |\vec{E}_s|^2 \rangle, \qquad (2.1)$$



Figure 2–1: Coordinate system of the experimental setup. The gray sphere is a sphere of radius q. The independent coordinates q, θ' and ϕ are the polar coordinates of the system with the base of the \vec{q} vector being the center. These are the conventional xray scattering coordinates with the angle 2θ representing the physical location of the detector (or a pixel of it). This figure is reproduced from Chapter 1 for ease of referral.

where \vec{E}_s is the scattered electric field[1]. Knowing the intensity means knowing how the sample scatters, which depends on its dynamics. Thus a theory linking scattered electric field and intensity would be linking the dynamics of the system with the scattered intensity measured.

To begin with, the direction of \vec{E} is ignored for two reasons. The first is that the radiation from the source comes from undulators, which produce linearly polarized radiation[8]. Thus the incoming beam may be assumed to point the same direction. The second is the fact that the scattering volume transverse lengths are much smaller than the distance from the sample to the detector. This means that the scattered field from each point source contribution may also be assumed to point the same direction. The vector superscript is dropped from now on because of these reasons.

Because the wavelength of the xrays are smaller than the size of an individual atom, the scattering is in the Thomson scattering regime, and the outgoing electric field is (chapter 3 of reference [10]):

$$E_{s}(\vec{R},t) = \frac{r_{0}}{R} e^{i(\vec{k}_{s}\cdot\vec{R}-\omega_{0}t)} \int_{V} e^{i\vec{q}\cdot\vec{r}} \delta\rho(\vec{r},t) E_{i}(\vec{r},t + \frac{k_{s}\cdot\vec{r}}{\omega_{0}}) d^{3}\vec{r}$$
(2.2)

Here \vec{R} refers to the vector pointing from the center of the sample to the detector. The deviation of density from the average, $\delta \rho = \rho - \langle \rho \rangle$, is used instead of ρ because there is no scattering from a uniform sample.

The system measured contains more interesting information in its fluctuations rather than its average quantities. In statistical mechanics, observing fluctuations is the same thing as calculating higher order moments of measured quantities. The measured quantity here is the scattered intensity as a function of \vec{q} . It turns out that calculating the second order moment is enough to describe the system here. This is because the statistics of the scattered field are Gaussian (by virtue of the central limit theorem). Any system governed by Gaussian statistics is completely described by its first and second order moments ([12]).

What is measured is the intensity for some time t. It is desired to calculate the intensity-intensity correlation function to compare different times t_1 and t_2 . However, it turns out that since the intensity is the square modulus of the electric field, it is then a second order moment of the electric field. Thus an intensityintensity correlation function is a fourth order moment of the electric field, and because this field is Gaussian, the fourth order moment can be written in terms of the first and second moments. For a completely coherent beam, using Wick's theorem[13](suppressing the \vec{q} dependence):

$$G_{2}(\vec{q},\tau) = \langle I(\vec{q},t)I(\vec{q},t+\tau)\rangle = (\epsilon_{0}c)^{2} \langle E^{*}(t)E(t)E^{*}(t+\tau)E(t+\tau)\rangle$$

$$= (\epsilon_{0}c)^{2} \left(\langle E^{*}(t)E(t)\rangle\langle E^{*}(t+\tau)E(t+\tau)\rangle + \langle E^{*}(t)E(t+\tau)\rangle\langle E(t)E^{*}(t+\tau)\rangle + \langle E^{*}(t)E^{*}(t+\tau)\rangle\langle E(t)E(t+\tau)\rangle \right)$$

$$+ \langle E^{*}(t)E^{*}(t+\tau)\rangle\langle E(t)E(t+\tau)\rangle \right)$$

$$= \langle I_{*}\rangle^{2} + (\epsilon_{0}c)^{2} |\langle E^{*}(t)E(t+\tau)\rangle|^{2}$$

$$(2.4)$$

$$= \langle I_s \rangle^2 + (\epsilon_0 c)^2 |\langle E^*(t) E(t+\tau) \rangle|^2$$

$$= \langle I_s \rangle^2 (1+|g_1(\tau)|^2)$$
(2.4)

where

$$g_1(\tau) = \frac{G_1(\tau)}{\langle I_s \rangle}$$
(2.5)

$$G_1(\tau) = \epsilon_0 c \langle E(t)^* E(t+\tau) \rangle.$$
(2.6)

Equation 2.5 defines the normalized electric field correlation function. The succeeding equation is referred to as the electric field correlation function¹. The scattered intensity, $\langle I_s \rangle$ can be computed from the scattering cross section, $\langle I_s \rangle = \frac{d\sigma}{d\Omega} \langle I_i \rangle$. The last term in equation 2.3 is zero because the complex phase $e^{-i\omega_0 t}$ averages to zero. Equation 2.4 is commonly referred to as the Siegert relation [14], (chapter 3 of reference [10]). Looking more closely at the electric field correlation and using the Born approximation (eq. 2.2):

$$\langle E^{*}(t)E(t+\tau)\rangle = e^{-i\omega_{0}\tau} \left(\frac{r_{0}}{R}\right)^{2} \int_{V} e^{i\vec{q}\cdot(\vec{r}_{2}-\vec{r}_{1})} \langle \delta\rho(\vec{r}_{1},t)\delta\rho(\vec{r}_{2},t+\tau)\rangle \langle E_{i}(\vec{r}_{1},t+\frac{\vec{k}_{s}\cdot\vec{r}_{1}}{\omega_{0}})E_{i}(\vec{r}_{2},t+\tau+\frac{\vec{k}_{s}\cdot\vec{r}_{2}}{\omega_{0}})\rangle d^{3}\vec{r}_{1}d^{3}\vec{r}_{2},$$
(2.7)

where the fact that the average of a product of independent parts is the product of their averages is used. Here, the correlation times of the electric field are assumed much shorter than that of the sample, so this is true.

Rewriting equation 2.7, one gets that:

$$\langle E^{*}(t)E(t+\tau)\rangle = e^{-i\omega_{0}\tau} \left(\frac{r_{0}}{R}\right)^{2} \int_{V} e^{i\vec{q}\cdot(\vec{r}_{2}-\vec{r}_{1})} \langle \delta\rho(\vec{r}_{1},t)\delta\rho(\vec{r}_{2},t+\tau)\rangle \Gamma_{i}(\vec{r}_{1},\vec{r}_{2},t+\frac{\vec{k}_{s}\cdot\vec{r}_{1}}{\omega_{0}},t+\tau+\frac{\vec{k}_{s}\cdot\vec{r}_{2}}{\omega_{0}}) d^{3}\vec{r}_{1}d^{3}\vec{r}_{2},$$
(2.8)

where:

$$\Gamma_i(\vec{r_1}, \vec{r_2}, t_1, t_2) = \langle E_i^*(\vec{r_1}, t_1) E_i(\vec{r_2}, t_2) \rangle.$$
(2.9)

 $^{^1}$ Notice the convention: Capital "G" used for a non-normalized function and lowercase "g" is used for a normalized correlation function

This function is also referred to as the mutual coherence function. For a perfectly coherent beam, the electric field is perfectly correlated in time and space. Thus the mutual coherence function becomes $\Gamma_i = \langle E_i \rangle^2 = \frac{\langle I_i \rangle}{\epsilon_0 c}$, where I_i is the incident intensity. With the extra assumption that the overall amplitude of the field varies slowly compared to τ , this gives:

$$\langle E^*(t)E(t+\tau)\rangle = e^{-i\omega_0\tau} \frac{\langle I_i\rangle}{\epsilon_0 c} \left(\frac{r_0}{R}\right)^2 \int_V e^{-i\vec{q}\cdot(\vec{r}_2-\vec{r}_1)} \\ \langle \delta\rho(\vec{r}_1,t)\delta\rho(\vec{r}_2,t+\tau)\rangle d^3\vec{r}_2 d^3\vec{r}_2$$

$$(2.10)$$

$$= e^{-i\omega_0\tau} \frac{\langle I_i \rangle}{\epsilon_0 c} \left(\frac{r_0}{R}\right)^2 S_2(-\vec{q},\vec{q},\tau)$$
(2.11)

where:

$$S_2(\vec{q}_1, \vec{q}_2, \tau) = \int_V e^{-i(\vec{q}_1 \cdot \vec{r}_1 + \vec{q}_2 \vec{r}_2)} \langle \delta \rho(\vec{r}_1, t) \delta \rho(\vec{r}_2, t + \tau) \rangle d^3 \vec{r}_2 d^3 \vec{r}_2.$$
(2.12)

This means that the correlation function $g_1(\tau)$ is:

$$g_1(\tau) = \frac{e^{-i\omega_0\tau} \langle I_i \rangle \left(\frac{r_0}{R}\right)^2}{\langle I_s \rangle} S_2(-\vec{q}, \vec{q}), \qquad (2.13)$$

$$= e^{-i\omega_0\tau} S_2(-\vec{q},\vec{q},\tau)$$
 (2.14)

where $\langle I_i \rangle$ and $\langle I_s \rangle$ are the intensity incident on and scattered off the sample, respectively. The substitution for Thomson scattering, $\langle I_s \rangle = \langle I_i \rangle \left(\frac{r_0}{R}\right)^2$ is made in the last step[5]. In this equation, the g₁ function is related to a Fourier transform of a density-density correlation. This in turn gives information about the fluctuations of the system.

2.2 Partially Coherent Xray Diffraction

The scattering of coherent xrays off of a sample give information related to a Fourier transform of a density-density correlation function. However, what if the xrays are not perfectly coherent over the scattering region considered?

It turns out that useful information may still be obtained. First of all, the integral of equation 2.10 can be collapsed into a three-dimensional integral. Here is a nice argument to explain this idea.

The system measured is disordered. Thus each piece of the system has no correlation with another piece of the system. A molecule will then correlate with only itself. Therefore, $\delta\rho(\vec{r_1},t)\delta\rho(\vec{r_2},t+\tau)$ will only be finite at some region proportional to the volume it occupies. In what is measured, particles are moving in some correlated fashion (such as flow and shear velocities), and then in some other random fashion (thermal motion, etc.). Therefore, the volume the particles that were scattering at an earlier time has moved at a later time due to the correlated movement. Assuming the particles are moving slow enough and that there are a lot of them, this integral may be approximated over different volumes. The first integral is over the scattering the radiation occupy. Because the velocity of the particles is very small, the limits of this integral may be changed. This then causes the dynamics to now be translationally invariant.

Evoking this translational invariance, the equation becomes:

$$\langle E^{*}(t)E(t+\tau)\rangle \approx e^{-i\omega_{0}\tau} \left(\frac{r_{0}}{R}\right)^{2} \int_{V_{1}} \int_{V_{2}} e^{i\vec{q}\cdot(\vec{r}_{2}-\vec{r}_{1})} \langle \delta\rho(0,t)\delta\rho(\vec{r}_{2}-\vec{r}_{1},t+\tau)\rangle \Gamma_{i}(\vec{r}_{1},\vec{r}_{2},t+\frac{\vec{k}_{s}\cdot\vec{r}_{1}}{\omega_{0}},t+\tau+\frac{\vec{k}_{s}\cdot\vec{r}_{2}}{\omega_{0}})d^{3}\vec{r}_{1}d^{3}\vec{r}_{2},$$

$$(2.15)$$

where V_1 and V_2 are the old volume and new volume respectively.

This approximation only remains correct if the effective mean volume displacement of the scattering is a very small fraction of the scattering volume. One can quantify this approximation as a time scale. The time scale τ_v is defined to be the time when a significant amount of the particles have exited the scattering volume. Further examination of this time scale will require understanding the dynamics of the system, which will be described in the next chapter.

The next part to solving this formula is to notice that the coherence function is actually also translationally invariant. If the coherence length is much smaller than the beam size, one can often approximate Γ by (chapter 3 of reference [10]):

$$\Gamma(\vec{r}_1, \vec{r}_2, 0, \tau) = \frac{1}{\epsilon_0 c} I(\frac{\vec{r}_1 + \vec{r}_2}{2}) \mu(\vec{r}_2 - \vec{r}_1, \tau), \qquad (2.16)$$

where

$$\mu(\vec{r}_2 - \vec{r}_1, \tau) = \frac{\Gamma(0, \vec{r}_2 - \vec{r}_1, 0, \tau)}{\Gamma(0, 0, 0, 0)}.$$
(2.17)

This equation is the same as saying that the coherence function is related to the product of a slowly varying intensity which depends on the absolute position and a slowly varying coherence factor which only depends on the relative distance. This makes sense, as coherence between two points from a close to parallel beam should be translationally invariant. The intensity is also slowly varying enough that it can be taken to depend on the coordinate $\frac{\vec{r_1}+\vec{r_2}}{2}$, to make the Jacobian of the coordinate transformation one.

Evaluating the integral gives:

$$\langle E^*(t)E(t+\tau)\rangle = e^{-i\omega_0\tau} \left(\frac{r_0}{R}\right)^2 \int_V \frac{I(\vec{u})}{\epsilon_0 c} d^3\vec{u} \int_V e^{i\vec{q}\cdot\vec{v}} \langle \delta\rho(0,t)\delta\rho(\vec{v},t+\tau)\rangle \mu(\vec{v},\tau)d^3\vec{v}$$
(2.18)
$$= e^{-i\omega_0\tau} \left(\frac{r_0}{R}\right)^2 V \frac{\langle I_i \rangle}{\epsilon_0 c} \int_V e^{i\vec{q}\cdot\vec{v}} \langle \delta\rho(0,t)\delta\rho(\vec{v},t+\tau)\rangle \mu(\vec{v},\tau)d^3\vec{v},$$
(2.19)

where $\vec{u} = \frac{\vec{r_1} + \vec{r_2}}{2}$ and $\vec{v} = \vec{r_2} - \vec{r_1}$. The correlation between a particle and itself at a later time varies on a much shorter length scale than the mutual coherence function, $\mu(\vec{v}, \tau)$. This is then pulled out of the integral to give:

$$g_1(\vec{q},\tau) = \epsilon_0 c \frac{\langle E^*(t)E(t+\tau)\rangle}{\langle I_s \rangle} = \epsilon_0 c \frac{\langle E^*(t)E(t+\tau)\rangle}{\langle I_i \rangle \left(\frac{r_0}{R}\right)^2}$$
(2.20)

$$= \sqrt{\beta} e^{-i\omega_0 \tau} V \int_V e^{i\vec{q}\cdot\vec{r}} \langle \delta\rho(0,t)\delta\rho(\vec{r},t+\tau) \rangle d^3\vec{r}$$
(2.21)

where:

$$\sqrt{\beta} = \mu(0,\tau). \tag{2.22}$$

Partial coherence adds a new factor β to the original correlation function. It is 1 for full coherence and 0 for no coherence. Generally, it makes more sense to remove the coherence factor β from the correlation and define g_1 to be:

$$g_1(\vec{q},\tau) = e^{-i\omega_0\tau} V \int_V e^{i\vec{q}\cdot\vec{r}} \langle \delta\rho(0,t)\delta\rho(\vec{r},t+\tau) \rangle d^3\vec{r}$$
(2.23)
From equation 2.4, the correlation function G_2 becomes:

$$\langle I(\vec{q}, 0)I(\vec{q}, \tau) \rangle = G_2(\vec{q}, \tau) = \langle I_s \rangle^2 (1 + \beta |g_1|^2)$$
 (2.24)

Where g_1 is defined in 2.23.

2.3 Solving g_1 for First Order Flow

There is one last piece to solve for in equation 2.23. This is the Fourier transform of the density-density correlation function:

$$\int_{V} e^{i\vec{q}\cdot\vec{r}} \langle \delta\rho(0,t)\delta\rho(\vec{r},t+\tau) \rangle d^{3}\vec{r}.$$
(2.25)

To solve for this, the dynamics of the system are broken into two parts: the random movement due to thermal vibrations (diffusion), and general flow. A general flow \vec{V} may be approximated by the expansion² :

$$\vec{V}(\vec{r}+d\vec{r}) = \vec{U} + \overleftarrow{\Gamma} \cdot d\vec{r} + O(dr^2), \qquad (2.26)$$

where:

$$\Gamma_{ij} = \frac{\partial V_i}{\partial x_j}.\tag{2.27}$$

Terms of order $|d\vec{r}|^2$ and higher are neglected. The term of order $d\vec{r}$ represents the velocity gradient. The simple case explained here is a linear shear in the plane perpendicular to the incoming beam. This linear shear is described by two

² Note: The shear matrix $\overleftarrow{\Gamma}$ is NOT to be confused with the coherence function, which is also Γ but is not a matrix.



Figure 2–2: Vector field representation of the velocity in terms of its shear term (first figure) and its flow term (second figure). Velocities along lines parallel to the drawn vectors are assumed to be the same and are not drawn for simplicity. The full velocity is the vector sum of the two terms.

parameters: the magnitude γ and the direction α_s of the shear gradient. This can

be seen in figure 2–2.

Then $\overleftarrow{\Gamma}$ becomes:

$$\overleftrightarrow{\Gamma} = \gamma \begin{bmatrix} \cos \alpha_s \sin \alpha_s & -\cos^2 \alpha_s & 0\\ \sin^2 \alpha_s & -\sin \alpha_s \cos \alpha_s & 0\\ 0 & 0 & 0 \end{bmatrix},$$
 (2.28)

where the proof is in Appendix A.

For particles undergoing diffusion with an average velocity $\overline{\vec{V}} = \vec{U} + \overleftarrow{\Gamma} \cdot \vec{r}$, a paper by G.G. Fuller[15], gives g_1 to be:

$$g_1(\vec{q},t) = e^{-\{\int_0^t [Dq'^2(t') + i\vec{U} \cdot \vec{q'}(t')dt'\}} \int \int \int d^3x \mathbf{I}(\vec{x}) e^{-i\int_0^t dt' \vec{q'}(t') \cdot \overleftarrow{\Gamma} \cdot \vec{x}}$$
(2.29)

$$\frac{d\vec{q'}}{dt} = -\Gamma^T \cdot \vec{q'}, \quad \vec{q'}(0) = \vec{q}$$
(2.30)

where D is the diffusion constant, $\overleftarrow{\Gamma}$ is the shear velocity gradient and $I(\vec{x})$ is the intensity of the incoming beam. Following Appendix A, the g_1 function becomes:

$$g_1(\vec{q}, t) = e^{-\frac{t}{\tau}} e^{iqUt\cos(\phi - \alpha_s)} \operatorname{sinc}(\omega_s t\sin\alpha_s) \operatorname{sinc}(\omega_s t\cos\alpha_s)$$
(2.31)

$$\omega_s = q\gamma \frac{a}{2}\sin(\phi - \alpha_s) \tag{2.32}$$

$$\tau = (Dq^2)^{-1} \tag{2.33}$$

where a is the scattering volume transverse length. Consequently, $\gamma \frac{a}{2}$ is the difference in velocity between the center and one of the edges of the scattering volume.

2.4 Homodyne and Heterodyne Correlation Functions

2.4.1 The Homodyne Correlation Function

What is measured eventually in the CCD detector is the number of photons received from the scattering, which is the intensity (time-average of Poynting vector). Computing an intensity-intensity correlation function is interesting. This gives(from equation 2.24):

$$G_2(\tau) = \langle I_s(t)^* I_s(t+\tau) \rangle = \langle I_s \rangle^2 \left(1 + \beta |g_1|^2 \right).$$
(2.34)

Then by using equation 2.31:

$$G_2(\tau) = \langle I_s \rangle^2 \left(1 + \beta e^{-\frac{2t}{\tau}} \operatorname{sinc}^2(\omega_s t \sin \alpha_s) \operatorname{sinc}^2(\omega_s t \cos \alpha_s) \right).$$
(2.35)

This is called the homodyne correlation function. Typically, the scattered intensity $\langle I_s \rangle$ can be computed by an average in time and space. Dividing this last equation by the scattered intensity squared, the result is:

$$g_2(\tau) = 1 + \beta e^{-\frac{2t}{\tau}} \operatorname{sinc}^2(\omega_s t \sin \alpha_s) \operatorname{sinc}^2(\omega_s t \cos \alpha_s).$$
(2.36)

This is called the normalized homodyne correlation function³. It is important to notice that this equation no longer depends on the flow velocity \vec{U} . This is due to the fact that the flow velocity is a complex phase factor lost on squaring.

2.4.2 The Heterodyne Correlation Function

The previous section showed that the homodyne correlation function gives no information about the flow velocity. However, the flow velocity can provide useful information about a system's dynamics. Clearly, it is a physical quantity that does affect the field in some way so there must be a way to measure it.

Looking again at equation 2.31, the complex phase is related to the Doppler shift of the frequency of the scattered electromagnetic wave. This appears as a phase in the representation of the electric field:

$$\vec{E}_s = \mathbf{A}(\mathbf{r})\vec{E}_i e^{-i\vec{q}\cdot\vec{U}t},\tag{2.37}$$

where \vec{U} is the flow velocity and A(r) represents the fraction of the field being scattered. The subscripts s and i refer to the scattered and incoming fields,

³ Note the convention: capital "G" and lower case "g" is used for a nonnormalized and normalized correlation function, respectively.

respectively. Having N scatterers close together all moving with the same flow velocity \vec{U} yields, by the superposition principle:

$$\vec{E}_s = N \mathcal{A}(\mathbf{r}) \vec{E}_i e^{-i\vec{q}\cdot\vec{U}t}.$$
(2.38)

A measurement of the intensity of this field would show it to be:

$$\langle I \rangle \sim |\vec{E}_s|^2 \sim N^2 |\vec{E}_i|^2. \tag{2.39}$$

It is clear that for such a system, there is a loss of the phase information through the measurement of the intensity.

This can be circumvented with the following idea. Suppose that half of the sample moved with some velocity \vec{U} and the other half remained still relative to the laboratory. The field would then be:

$$\vec{E}_s = \frac{N}{2}\vec{E}_i e^{-i\vec{q}\cdot\vec{U}t} + \frac{N}{2}\vec{E}_i.$$
(2.40)

The intensity of the field would then be:

$$\langle I \rangle \sim |\vec{E}_s|^2 = 2\left(\frac{N}{2}\right)^2 |\vec{E}_i|^2 + \left(\frac{N}{2}\right)^2 |E_i|^2 \left(e^{i\vec{q}\cdot\vec{U}t} + e^{-i\vec{q}\cdot\vec{U}t}\right)$$

$$= 2\left(\frac{N}{2}\right)^2 |\vec{E}_i|^2 + 2\left(\frac{N}{2}\right)^2 |\vec{E}_i|^2 \cos(\vec{q}\cdot\vec{U}t).$$
(2.41)

Clearly, by simply adding a reference beam, information about the phase in the electromagnetic wave can be obtained through a correlation function in time.

Now what happens by the addition of a reference sample? An easy way to see what happens is to go back to equation 2.5:

$$g_1(\vec{q},\tau) = \frac{\langle E^*(t)E(t+\tau)\rangle}{\langle I_s\rangle}.$$
(2.42)

The scattered electric field is broken up as a contribution from the reference and the sample:

$$E(t) = E_r(t) + E_s(t).$$
 (2.43)

The correlation function g_1 becomes:

$$g_{1}(\vec{q},\tau) = \frac{1}{\langle I_{s} \rangle} \langle (E_{s}(t) + E_{r}(t))^{*} (E_{s}(t+\tau) + E_{r}(t+\tau)) \rangle$$

$$= \frac{1}{\langle I_{s} \rangle} (\langle E_{s}^{*}(t)E_{s}(t+\tau) \rangle + \langle E_{s}^{*}(t)E_{r}(t+\tau) \rangle + \langle E_{r}^{*}(t)E_{s}(t+\tau) \rangle + \langle E_{r}^{*}(t)E_{r}(t+\tau) \rangle)$$

$$= \frac{1}{\langle I_{s} \rangle} (\langle E_{s}^{*}(t)E_{s}(t+\tau) \rangle + \langle E_{r}^{*}(t)E_{r}(t+\tau) \rangle).$$

$$(2.44)$$

Here, the terms $\langle E_s^*(t)E_r(t+\tau)\rangle$ and $\langle E_r^*(t)E_s(t+\tau)\rangle$ yield zero due to the fact that there are no correlations between both samples. Let $\langle I_s\rangle = \langle I_{s,ref} + I_{s,sam}\rangle$, where $\langle I_{s,ref}\rangle$ and $\langle I_{s,sam}\rangle$ are the the scattered intensity from the reference and the sample, respectively. Also, define:

$$x(\vec{q}) = \frac{\langle I_{s,sam} \rangle(\vec{q})}{\langle I_{s,ref} \rangle(\vec{q}) + \langle I_{s,sam} \rangle(\vec{q})}.$$
(2.45)

Using equation 2.23 and noticing now that for the reference and the sample, the normalization factor is $\langle I_{s,ref} \rangle$ and $\langle I_{s,sam} \rangle$, respectively, the equation becomes⁴:

$$g_1(\vec{q},\tau) = (xg_{1s}(\vec{q},\tau) + (1-x)g_{1r}(\vec{q},\tau))$$
(2.46)

where g_{1s} and g_{1r} are the g_1 functions of the scattering of an experiment assuming that the sample or the reference were occupying the whole scattering volume, respectively.

By using equation 2.24 to get the heterodyne G_2 function⁵ :

$$\begin{aligned} \mathbf{G}_{2}(\vec{q},\tau) &= 1 + \beta |\mathbf{g}_{1}|^{2} \\ &= 1 + \beta \left\{ (x\mathbf{g}_{1s}^{*} + (1-x)\mathbf{g}_{1r}^{*})(x\mathbf{g}_{1s} + (1-x)\mathbf{g}_{1r}) \right\} \\ &= 1 + \beta \left\{ x^{2} |\mathbf{g}_{1s}|^{2} + \left\{ x(1-x)\mathbf{g}_{1s}^{*}\mathbf{g}_{1r} + (x(1-x)\mathbf{g}_{1s}^{*}\mathbf{g}_{1r})^{*} \right\} + (1-x)^{2} |\mathbf{g}_{1r}|^{2} \right\} \\ &= 1 + \beta \left\{ x^{2} |\mathbf{g}_{1s}|^{2} + 2x(1-x)Re\left(\mathbf{g}_{1s}^{*}\mathbf{g}_{1r}\right) + (1-x)^{2} |\mathbf{g}_{1r}|^{2} \right\}.\end{aligned}$$

In the experiments described here, the reference sample is static over the measurement time, therefore the correlation function vanishes to some constant number. The G_2 correlation function then simplifies to [16]:

$$G_2(\vec{q},\tau) = 1 + \beta \left((1-x)^2 + 2x(1-x)Re\left(g_{1s}(\vec{q},\tau)\right) + x^2 |g_{1s}(\vec{q},\tau)|^2 \right)$$
(2.47)

⁴ From now on, the \vec{q} dependence of x will be supressed

⁵ Note, β is assumed to be the same for both the sample and reference. This approximation applies to the experiments done here but is not necessarily true (i.e. the integrals are carried over different portions of the scattering volume where β may change).

The importance of this equation cannot be over-emphasized. If one remembers from previous derivations, the intensity-intensity correlation function of only the sample is related to the modulus squared of the electric field correlations. However, by introducing a reference sample, the new intensity-intensity correlation function now depends in part on the electric field correlation function directly. This is a really powerful technique. This means that inserting a known reference and making x small enough (but not zero) provides a direct measurement of the real part of the electric field correlation functions.

Recalling what the electric field correlation function of the sample is and taking the real part:

$$Re[g_1(\vec{q},t)] = e^{-\frac{t}{\tau}} \cos(qUt\cos(\phi - \alpha_s))\operatorname{sinc}(\omega_s t\sin\alpha_s)\operatorname{sinc}(\omega_s t\cos\alpha_s).$$
(2.48)

One can see that if the frequency $qUt \cos(\phi - \alpha_s)$ is large enough that this function is an oscillatory function enveloped by a decay. The frequency is related to the uniform flow velocity. Thus by just counting the number of oscillations in a time period provides an estimate of the flow velocity.

2.5 Speckle Statistics and Averaging

The experiments here do not have infinite time over which to do the averaging. Therefore it is necessary to examine the statistics of the time average more carefully.

2.5.1 Simple Time Average

The Fourier transform of the intensity at one pixel is:

$$I(t) = \int e^{i\omega t} I_{\omega} d\omega. \qquad (2.49)$$

Now what happens when the average $\langle I^*(t)I(t+\tau)\rangle_t$ is taken? This gives:

$$\langle I(t)I(t+\tau)\rangle_t = \langle \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{i(\omega-\omega')t} e^{-\omega\tau} I_{\omega}^* I_{\omega'} d\omega d\omega \rangle_t$$

$$= \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \delta(\omega'-\omega) e^{-i\omega\tau} I_{\omega}^* I_{\omega'} d\omega d\omega'$$

$$= \int_{-\infty}^{\infty} e^{-i\omega\tau} |I_{\omega}|^2 d\omega,$$

$$(2.51)$$

where the last equation is the Wiener Khinchin theorem [7]. From this equation, it is apparent that averaging over the intensity-intensity correlation function over enough time results in a delta function. Given finite time however, this is not the case and must be examined further. Fortunately, by understanding better how the errors arise from these averages, tricks may be used to improve the results. However, before understanding the errors, speckle must be well understood.

2.5.2 Speckle

As was seen from chapter 1, interference effects can be observed by coherent radiation. In general, it was seen that partially coherent radiation also provides interference effects, but where amplitude of this interference is now "damped" by a factor $\sqrt{\beta}$. More specifically, at any point in a detector, the intensity can be seen as a sum of two parts:

$$I(\vec{q},t) = I_{avg}(\vec{q}) + \sqrt{\beta}\delta I(\vec{q},t)$$
(2.52)

The first term in this equation is the average intensity that would be observed if the beam was completely incoherent and the second term is the interference term δI times the coherence factor $\sqrt{\beta}$ ($0 > \sqrt{\beta} > 1$ for partial coherence). From the first chapter, it was seen that the interference term $\delta I(\vec{q}, t)$ fluctuates between $\pm I_{avg}(\vec{q})$. To understand speckle better, a new variable is defined:

$$\delta s(\vec{q},t) = \frac{\delta I(\vec{q},t)}{I_{avg}(\vec{q},t)}.$$
(2.53)

This term δs is the contribution of the speckle. It varies from -1 (completely destructive interference) to 0 (no interference) to 1 (completely constructive interference). It is now seen that the intensity at any time t is:

$$I(\vec{q},t) = I_{avg}(\vec{q}) \left(1 + \sqrt{\beta}\delta s(\vec{q},t)\right)$$
(2.54)

This will aid in the analysis of the calculation of the averages.

2.5.3 Introducing The Spatial Average

Now that speckle is understood, the averaging method can be explained in simple terms. The intensity-intensity correlation function is rewritten in terms of equation 2.54:

$$\langle I(\vec{q},t)I(\vec{q},t+\tau)\rangle_t = I_{avg}^2 \left(1 + \sqrt{\beta} \left(\langle \delta s(\vec{q},t) + \delta s(\vec{q},t+\tau)\rangle_t\right) + \beta \langle \delta s(\vec{q},t)\delta s(\vec{q},t+\tau)\rangle_t\right)$$
(2.55)

Now, as the system measured changes configurations, the speckle term δs fluctuates in time t for a pixel at \vec{q} . Thus the terms involving $\langle \delta s(\vec{q},t) \rangle_t$ should vanish when averaged over a long enough time, and one should be left with:

$$\langle I(\vec{q},t)I(\vec{q},t+\tau)\rangle_t = I_{avg}^2 \left(1 + \beta \langle \delta s(\vec{q},t)\delta s(\vec{q},t+\tau)\rangle_t\right).$$
(2.56)

However, if the system is not observed over a long enough time, two things occur. Firstly, the $\langle \delta s(\vec{q}, t) \rangle_t$ terms do not vanish. Secondly, the second term of equation 2.56 will have a non-negligible error. This can be fixed by adding in a spatial average.

One can perform the average over a small area $\Delta q_x \Delta q_y$ provided that the average intensity $I_{avg}(\vec{q})$ and the speckle dynamics do not vary too much. By looking at the results obtained, one can see if this assumption makes sense. Averaging over slightly different \vec{q} 's is then equivalent to averaging over different speckle patterns. The average then looks as follows:

$$\langle I(\vec{q},t)I(\vec{q},t+\tau)\rangle_{\vec{q},t} = I_{avg}^2 \left(1 + \sqrt{\beta} \left(\langle \delta s(\vec{q},t) + \delta s(\vec{q},t+\tau)\rangle_{\vec{q},t}\right) + \beta \langle \delta s(\vec{q},t)\delta s(\vec{q},t+\tau)\rangle_{\vec{q},t}\right)$$

$$(2.57)$$

where the average is now done over many \vec{q} values.

2.5.4 Error Analysis

As both these averages are finite, this introduces some error. It is important to note that this error is not due to the intensity measurements (which is of a much higher accuracy), but due to the simple fact that the average involves a small number of points. The best way to understand this error is to view it in terms of speckle. Speckle is loosely defined to be regions of local maxima, which is due to strong constructive interference. According to Sutton's review on XIFS[17], this error is proportional to $\frac{1}{\sqrt{N_s}}$, where N_s is the number of speckles observed. As speckle is easily observed and counted in the CCD camera, this error can easily be observed and estimated. The error can be seen easier by rewriting equation 2.57 as:

$$\langle I(\vec{q},t)I(\vec{q},t+\tau)\rangle_t = I_{avg}^2 \left(1 + \beta \left(\frac{1}{\sqrt{\beta}} \left(\langle \delta s(\vec{q},t) + \delta s(\vec{q},t+\tau)\rangle_{\vec{q},t}\right) + \langle \delta s(\vec{q},t)\delta s(\vec{q},t+\tau)\rangle_t\right)\right).$$

As the error in the $\langle \delta s(\vec{q}, t') \rangle_t$ terms is $\frac{1}{\sqrt{N_s}}$, this means that the correlation function, which really measures $\langle \delta s(\vec{q}, t) \delta s(\vec{q}, t + \tau) \rangle_{\vec{q},t}$ will be slightly too high or too low by an order of $\frac{1}{\sqrt{\beta N_s}}$. In the experiments here, β is on average 0.3 and visual analysis shows N_s to range from 100 to 1000. This means that the error in the correlation function should be expected to be from 6% to 18%. It is important to note that this error comprises of an error constant in time τ and another error changing in time τ . The constant error will cause analysis over different portions of the data to differ by this error. However, the error changing in time τ is correlated with the last term in eq 2.58 and is a bit more complicated to figure out. However, further analysis of this error is beyond the scope of this thesis, and will not be discussed here. The importance of this conclusion relevant to this research is to justify the appearance of strange correlated errors, which will be seen later on in this thesis.

2.5.5 The Spatial Average: The Two-Time Correlation Function

Recalling from equation 2.57, before obtaining the correlation function, a spatial average and time average need to be carried out. The spatial average is



Figure 2–3: Sample two-time correlation matrix from 60% \uparrow 1 heterodyne 3 and homodyne 3 data (see appendix C for measurement nomenclature), respectively from left to right. Color indicates height.

computed as follows:

$$G_2(\vec{q_0}, t_1, t_2) \approx \frac{1}{N_q} \sum_{\vec{q_i}} I^*(\vec{q_i}, t_1) I(\vec{q_i}, t_2), \qquad (2.58)$$

where N_q is the number of points averaged over.

This intermediate step is what is called the two-time correlation function. It is important to recognize that it is a matrix of the products of intensities at different times t_1 and t_2 averaged over space. Two example two-time correlation matrices from the data are shown in figure 2–3. The axes represent the times t_1 and t_2 . The time difference axis $\tau = t_2 - t_1$ and the average time $t = \frac{t_2+t_1}{2}$ are marked in black to aid the eye.

Aside on the error

Looking at figure 2–3, one can see bumps along the diagonal for the heterodyne two-time correlation matrix. The bumps are not apparent in the homodyne



Figure 2–4: Sample two-time correlation matrix and its corresponding $g_2(\vec{q}, \tau)$ for a measurement. More specifically, this two-time correlation matrix is calculated for a portion of a measurement of $0\% \downarrow 1$, homodyne mode 2 (See Appendix C for measurement details).

data because they occur on a larger time scale. This is the correlated error discussed in equation 2.58. This will cause each of the computations of the $g_2(\tau)$ functions to be consistently off by some parameter.

2.5.6 The Time Average

Time Invariant System

Following the spatial average, is the time average. This average consists of averaging over points with the same value τ . This is the same as summing up all points along lines parallel to the $t_1 = t_2$ diagonal (or t axis as seen in figure 2–3), for each τ . Mathematically, the following sum is taken:

$$G_2(\vec{q},\tau) = \frac{1}{N_t} \sum_{t_i} G_2(\vec{q},t_i,t_i+\tau), \qquad (2.59)$$

where N_t is the number of points summed. An example of such a sum is demon-



Figure 2–5: Example of a two-time correlation matrix of time-dependent data. This is from the same data, but taken over larger frames.

strated in figure 2–4.

Time-Dependent System: Limiting the Time Window

One problem encountered in this research is that the system is not in equilibrium. An example of a two-time correlation function that does not change in time is shown in figure 2–5. By eye, one can easily notice that lines of constant $t_2 - t_1$ have more than some oscillatory behaviour described in equation 2.50. This is due to the fact that the system is changing in time, and that the intensity-intensity correlation function is no longer time invariant. However, the system is changing slowly enough that it may be assumed to be time invariant for small enough times. This time interval is referred to as the window, and is represented by the variable ww, as can be seen in figure 2–6. From this same reasoning, one can also reason that any value of τ over large values of ww will not be able to describe the dynamics of the system sufficiently.



Figure 2–6: The two-time correlation matrix with a region selected. The height along t_2 is denoted as ww. The dimension along t_1 is denoted as r1. The lower left hand corner of the selection's t_1 coordinate is known as t_{off}

One can imagine solving this problem as follows. Although the system is not in equilibrium, it is varying slowly enough that at each instant t_0 , it is in quasiequilibrium between times $t_0 - \frac{ww}{2}$ and $t_0 + \frac{ww}{2}$. Thus computing the correlation function for this small range of time produces an intensity-intensity correlation function describing the dynamics of the system as a function of t_0 . This can now provide information about the time-evolution of the system!

To develop this into a computation algorithm, one can define one more variable, r1, which is the range of τ which to average over. Now, instead of doing an average over all times t in the equation 2.50, an average from times $t_0 - \frac{ww}{2}$ to $t_0 + \frac{ww}{2}$ for times $0 < \tau \le r1$ will be done. The area now averaged over in the two time correlation function is the window that seen again in figure 2–6.

This method gives good results for slowly varying non-equilibrium dynamics.

2.6 Experimental Details

2.6.1 Setup

The experiment is set up at the origin of the coordinate system and can be seen in figure 2–1. The rubber sample was placed in a home-made stressstrain device which could stretch and hold the rubber at a desired constant elongation[18]. The apparatus was brought to the Advanced Photon Source (APS) at Argonne National Laboratory (Argonne, IL, USA). The beam size is $15\mu m \times 15\mu m$ and was collimated by polished slits 0.68 m from the sample. A deep-depletion CCD camera (PI 1152 × 1242, 22.5 μm resolution) was placed 2.8 m from the sample. The wavelength of the source is 1.62 Å. The monochromator used was a Ge(111) crystal, with energy contrast $\frac{\delta\lambda}{\lambda} = 3.2 \times 10^{-4}$.

From equation 1.3, the transverse coherence length of the beam is $L_T \approx 3.5$ μm . The transverse beam size is 15 μm , as mentioned above. This means that the transverse lengths of the scattering volume is approximately 4 times the transverse coherence length, and some resolution in speckle should be lost.

From equation 1.3.2, the longitudinal coherence length of the beam is $L_L \approx 0.25 \ \mu m$. However, for scattering at small angles and a sample thickness e, $(2\theta < 10^{-4} rad)$ the maximum path length difference of the scattered waves is $2e\theta^2$ [9]. The sample's thickness is less than 2 mm. This leaves the maximum wave path length difference to be $< 0.04 \ nm$. This is much smaller than the longitudinal coherence length. So no decrease in the amplitude of the speckle is expected.

In total, this means that the total scattering volume is 4 coherence volumes in size. The coherence factor, β scales as the inverse of the coherence volumes [17]. This is equal to 0.3 in the experiments here. This says that the scattering volume is a little bigger than the size of 3 coherence volumes, which agrees with the estimate here.

The static reference sample used for the heterodyne signal is a powder of fumed silica (Aerosil(200), 1 mm thick, placed immediately upstream of the sample. The reader is referred to reference [9] for more details on the experimental setup.

2.7 The Measurements

The measurements were organized in terms of stretches. The rubber is stretched at different elongations (strains): 20%, 40%, and 60% its initial length and allowed sufficient time to reach equilibrium during each elongation. The sample is held together with clamps 25 mm apart in length. While holding the rubber fixed, the clamps were then displaced symmetrically to 30, 35, and 40 mm consecutively (i.e. increments of 20% the initial length). A strain gauge simultaneously took readings of the strain of the sample, which were logged. To reach each elongation, a machine either stretched or relaxed the rubber to the desired strain. Elongations resulting from a stretch from a smaller elongation or a relaxation from a longer elongation are referred to as \uparrow ("up") and \downarrow ("down") stretches respectively. A repeated stretch will be succeeded by the number 2. For example, the second 40% "up" stretch will be referred to as 40% \uparrow 2. At each elongation, six different measurements were taken, alternating in homodyne and heterodyne mode for different exposure times. Each measurement for a particular stretch is referred to by the measurement type and the scan number of the measurement. For example, the third heterodyne measurement for $20\% \downarrow$ refers to the last heterodyne measurement for that stretch. During each measurement, the time elapsed is referred interchangeably as frames or time in seconds. A frame is a snapshot in time of the speckle. Each frame was taken 2.1s after the other in the homodyne mode, and 2.5s after the other in heterodyne mode. A summary of everything described here can be found in Appendix C for quick reference.

2.8 Summary

In summary, the tools necessary to examine the data from the measurement have been explained. In homodyne mode, one should expect an intensity-intensity correlation of the form equation 2.36. In heterodyne mode, one should expect an intensity-intensity correlation function of the form 2.47. Due to the timedependent nature of the sample, the correlation function is averaged over a small number of times. In order to increase the accuracy of the calculations, an average over wave vectors is also calculated. It should not change the correlation function so long as the intensity-intensity correlation function does not vary too much over the wave vectors averaged.

CHAPTER 3 Results & Analysis

To recapitulate from the last chapter, a theory linking the measurement and the dynamics of the system was derived. It was shown that some minor modifications and adjustments are necessary before obtaining the correlation function. The first is to include an average of the intensity-intensity correlation function over pixels to help compensate for the fact that the averaging is done over a small times. The second is to limit the average of this correlation function over time.

The heterodyne data is analysed with these modifications, and its fits are described in full detail. As a supplemental section, fits of the homodyne data are also described. Before moving on to the heterodyne data, the partitioning of the data for the averaging needs to be described more thoroughly.

3.1 Partitioning and Selecting Pixels

Before computing the actual correlation functions, an initial analysis of how to partition the data is described. Initial analysis shows that the correlation functions from equations 2.36 and 2.47 do not vary significantly over a small enough area of the detector. As was seen before, it is necessary to average over a few pixels in order to have a better resolution of the g_2 correlation functions. Therefore, the pixels are classified into appropriate bins. To make these bins, the scattering



Figure 3–1: 30×30 Partition Map of the Pixels. The black box represents a mask.



Figure 3–2: Coordinate system of the experimental setup. The gray sphere is a sphere of radius q. The independent coordinates q, θ' and ϕ are the polar coordinates of the system with the base of the \vec{q} vector being the center. These are the conventional xray scattering coordinates with the angle 2θ representing the physical location of the detector (or a pixel of it). This figure is again reproduced from Chapter 1 ease of referral.

vector \vec{q} is divided into spherical coordinates¹ $|\vec{q}|$, ϕ and θ' . The scattering geometry is again included in this chapter and can be seen in figure 3–2. Again, this figure is the same as in the first chapter and has been reproduced for ease of viewing. In the small angle scattering (SAXS) region, θ' is close to zero, and may be ignored. The coordinates are then reduced to 2 dimensional polar coordinates, qand ϕ . By trial and error, it was decided to break up this whole area into a 30 × 30 grid of q and ϕ coordinates. These are the bins.

Each of the 30 mean q values and mean ϕ values are then given a unique number 1-30 to distinguish them, in order of increasing values. This means that each bin is represented by a pair of numbers representing which mean q and ϕ is being referred to. A schematic representation of the bins can be seen in figure 3–1. Each white area in the grid represents a selection of pixels from the CCD camera. For example, the third ring of white pixels contains equal numbers of q vectors whose magnitude varies from $3.61 \cdot 10^{-3} \text{ Å}^{-1} < |\vec{q}| < 4.54 \cdot 10^{-3} \text{ Å}^{-1}$, so the mean q value of this q ring would be the average of the extremes, or $4.07 \cdot 10^{-3} \text{ Å}^{-1}$.

The intensity-intensity correlation functions are then averaged over these bins. A representation of the number of pixels per bin can be seen in figure 3–3. Each bin has a mean q and ϕ value. The horizontal axis is the corresponding q number for each bin, and the vertical axis is the corresponding ϕ number for the same bin. For simplicity, the q and ϕ values have been numbered 1 through 30. The color of each square in the grid represents the value of the number of pixels at the

¹ The angle θ' is used here to distinguish this angle from the scattering angle 2θ



Figure 3–3: A color representation of the number of pixels per bin. The horizontal axis represent the radial component of \vec{q} in figure 3–1. The vertical axis represents the angular component of the same figure. A region in white means that the corresponding value of q and ϕ is not in the detector.

corresponding bin. A value of white signifies that such a combination of q and ϕ values does not appear in the detector. For example, one can see that for the first ring of q in figure 3–1, about less than half of the possible ϕ values are not blocked by the mask. This is reflected by the fact that less than half of the squares in the row for the first q value in figure 3–3 are non-white. Also, one sees that the areas of the bins seem to increase as q increases. This is reflected again in figure 3–3 by the fact that the value for the number of pixels are increasing for each bin (see legend for values).

This number of partitions is chosen for two reasons. The first is that the correlation functions were estimated not to change appreciably over the ranges of q and ϕ averaged over. The second reason is that the areas were still big enough to obtain an accurate average to obtain the correlation function, as described in the

previous chapter. Some bins had very few pixels and could not be appropriately analyzed. What was done is to remove those bins with less than 1000 pixels from the analysis.

3.2 The Heterodyne Correlation Function

To recapitulate, the heterodyne correlation function, for the case of an exponential correlation function, looks like this:

$$g_2(\vec{q},\tau) - 1 = \frac{\langle I(\vec{q},t)I^*(\vec{q},t+\tau)\rangle}{\langle I\rangle^2} - 1$$
(3.1)

$$g_2(q,\phi,t) - 1 = \beta(1-x)^2 + x^2\beta\operatorname{sinc}^2(\omega_s t \cos \alpha_s)\operatorname{sinc}^2(\omega_s t \sin \alpha_s)e^{-\frac{2t}{\tau}} \quad (3.2)$$

$$+2x(1-x)\beta\cos(\omega_f t)\operatorname{sinc}(\omega_s t\cos\alpha_s)\operatorname{sinc}(\omega_s t\sin\alpha_s)e^{-\frac{t}{\tau}}$$

$$\omega_f = \vec{q} \cdot \vec{U}$$
(3.3)

$$\omega_s = q\gamma \frac{a}{2}\sin(\phi - \alpha_s) \tag{3.4}$$

$$\tau = \frac{1}{Dq^2} \tag{3.5}$$

In the experiments, x is typically about 0.1, which means that $x^2 \approx 10^{-2}$ and $x(1-x) \approx 9 * 10^{-2}$. Thus the x^2 term is 1 order of magnitude lower than the x(1-x) term, so it is ignored.

The heterodyne correlation function then becomes:

$$g_2(q,\phi,t) = 1 + \beta(1-x)^2$$

$$+2x(1-x)\beta\cos(\omega_f t)\operatorname{sinc}(\omega_s t\cos\alpha_s)\operatorname{sinc}(\omega_s t\sin\alpha_s)e^{-\frac{t}{\tau}}, \quad (3.7)$$

where again, the values ω_f , τ , and ω_s are described in the previous equations. Before proceeding with any analysis, it is important to observe the effect of each



term of the function. The terms are plotted in figure 3–4. There are three time

Figure 3–4: The heterodyne function fit components. The red is the curve with just the diffusion component. The green is the cosine component multiplied with the diffusion component. The blue is the sinc component multiplied with the diffusion component. The black is the full g₂ correlation function. The parameters used: $\beta(1-x)^2 = 0.35$, $2x(1-x)\beta = 0.05$, $\omega_f = \frac{\pi}{40}$, $\omega_s = \frac{51\pi}{100}$, $\tau_d = 200$, $\alpha_s = 0$.

constants to worry about here: τ_d , the diffusion time constant, $\tau_f = \frac{\pi}{\omega_f}$ the period of the term due to flow, and $\tau_s = \frac{\pi}{\omega_s}$ period of the term due to shear. All three terms depend on the position in the detector in the following manner:

$$\tau_d \sim \frac{1}{q^2} \tag{3.8}$$

$$\tau_f \sim \frac{1}{q\cos\phi} \tag{3.9}$$

$$\tau_s \sim \frac{1}{q\cos\phi} \tag{3.10}$$

This means that as q increases, the g_2 correlation function decays more rapidly, due to the diffusion and the shear terms. However, at small q, the oscillatory behaviour of the function becomes too slow to measure. It turns out that in this case, the shear time constant is small enough that it can be neglected in the heterodyne data. However, it is not negligible in the homodyne data, which will be briefly described near the end of this chapter.

3.3 Simple Example: 60% \uparrow , Heterodyne **3**

Before proceeding with fits for the whole data set, a portion of 60% \uparrow heterodyne 3 is analysed. Recalling how the measurements were taken from the last chapter, this means that the rubber was stretched from its previous elongation of 40% to 60%, and sat there for a little over an hour as data was collected. As this is the third heterodyne measurement, this measurement starts a long time after the last stretching occurred. Thus it is expected that the rubber is reaching equilibrium and that the dynamics should not be too fast. However the stress strain curve is still changing with time, which signifies that the system is not yet in equilibrium. This implies the presence of flow. It turns out it was successfully measurable which is described here.

Figure 3–5 demonstrates a sample two-time correlation matrix for a portion of measurement 60% \uparrow heterodyne 3. The velocity is rather constant, which makes it a good example to start with. With a simple fitting routine, the data is fit to the following function:

$$g_2(q,\phi) = A + Be^{-\frac{t}{\tau}}\cos(\omega t) \tag{3.11}$$



Figure 3–5: A portion of the two-time correlation matrix for measurement 60% \uparrow heterodyne 3 at coordinates $q(10) = 0.010747 \text{\AA}^{-1}$, $\phi(15) = 216.5^{\circ}$

for each q and ϕ combination. The exponential function is added to account for a decay of the correlation function to allow for better fits.

What is done next is to apply a fitting routine for q-ring 10. The fitting routine is done using a non-linear least squares fit, which minimizes a χ^2 . A few sample fits in figure 3–6 are shown for q-ring 10 ($q(10) = 1.07 \times 10^{-2} \text{Å}^{-1} \pm 9.3 \times 10^{-4} \text{Å}^{-1}$). As can be seen from the figure, the fits reproduce the data very well. Since there are thousands of fits during the course of this thesis, the χ^2 will not be discussed in detail as this would detract from explaining the nature of the results. Next, it is observed that the fitted ω parameter should follow the simple relation:

$$\omega = \vec{q} \cdot \vec{U} = qU\cos(\phi - \alpha_f) \tag{3.12}$$

where \vec{U} is the flow velocity and \vec{q} is the usual scattering vector. Thus, plotting $\omega(\phi)$ should give a cosine function, which is what is measured. The frequency, $\omega(\phi)$



Figure 3–6: Fits for the g_2 correlation functions at $q(10) = 1.07 * 10^{-2}$ Å. The value ϕ increases from left to right, top to bottom from 173° to 285°. The black line is the data and the red curve is the fitted curve. The horizontal axis specifies the time difference τ and the vertical axis is the intensity-intensity correlation function. Each g_2 is obtained from an average in t of a specific two-time correlation matrix, as seen in figure 3–5.



Figure 3–7: Fit results for a sample fit of the ω parameter for constant q. It is clear that it obeys a $\cos(\phi - \phi_0)$ behaviour. The black curve points are the fitted omega parameters and the red curve is the fit of the black curve to equation 3.11



Figure 3–8: Fit results of a sample fit of the ω parameter for constant ϕ . A nice linear relationship is obtained which supports equation 3.13

can be seen in figure 3–7. The black curve is the data and the red curve is the data fit to:

$$A\cos(\phi - \phi_0) \tag{3.13}$$

where: $A = |\vec{q}|U, q = 1.07 * 10^{-2} \text{\AA}^{-1}, U \approx 27.1 \frac{\text{\AA}}{s}$ and $\phi_0 = 261^{\circ}$.

In the same way that plotting $\omega(\phi)$ should give a cosine function, a linear function is expected by plotting $\omega(q)$. This can be seen in figure 3–8, for $\phi = 185^{\circ}$. Here, the red curve is just the linear function:

$$Aq (3.14)$$

where $A = 16.62 \frac{radians}{(\text{\AA} \cdot frame)} = 6.65 \frac{rad}{\text{\AA} \cdot s}$.

Using the fact that A should be $A = U \cos(\phi - \phi_0)$ and that $\phi_0 = 260.9^{\circ}$ (from the previous fit), the flow velocity becomes:

$$U = \frac{A}{\cos(\phi - \phi_0)} \approx 65.98 \frac{\text{\AA}}{frame} = 26.4 \frac{\text{\AA}}{s}$$

which is in pretty good agreement with equation 3.3, with a 2.6% difference. In conclusion, a flow velocity of $26.7 \pm 5\% \frac{\text{\AA}}{s}$ has been successfully measured.

Again, looking at equation 3.12, one can notice a potential problem. The maximum frequency (when $\phi = \phi_0$) $\omega_{max} = \omega(q, \alpha_f)$ increases with increasing q. Thus there will be regimes where either the oscillation frequency will be too fast or too slow to measure. The low regime is when the oscillation frequency reaches a frequency faster than $\pi \frac{rad}{frame} = 1.3s^{-1}$. The upper regime (assuming the data are only valid for 25 frames) is $\pi \frac{rad}{25frames} = 5.0 * 10^{-2}s^{-1}$. Consequently, data outside of this range are disregarded.



Figure 3–9: Two-time correlation matrix for measurement 60% \uparrow heterodyne 3

Since q ranges between $4.0 \cdot 10^{-3} \text{\AA}^{-1} < q < 3.0 \cdot 10^{-2} \text{\AA}^{-1}$, flow velocities are measurable in the range of:

$$2\frac{\dot{A}}{s} < U < 5000\frac{\dot{A}}{s}.$$
 (3.15)

3.4 Beginning A Full Scale Fit

The last fit procedure was carried out over a small range of frames to compute a flow velocity. One can repeat this procedure over different sets of times to obtain a flow velocity for each time. This iterative procedure is carried out for the whole $60\% \uparrow 1$ data.

Figure 3–9 shows the full two-time correlation function for one bin of measurement 60% \uparrow heterodyne 3. One can notice by eye that the dynamics of the system have a time-dependent nature. This is due to the fact that the oscillation period changes as the time t_1 increases. The same procedure was done to fit the flow velocities and angles as described before for g_2 correlation functions averaged



Figure 3–10: Time dependent flow velocities for measurement 60% \uparrow heterodyne 3 over different portions of the two-time correlation matrix. The results of the flow velocity and flow angles can be seen in figures 3–10 and 3–11. One can see that the flow velocity (figure 3–10) has a rather bumpy nature.

3.5 The Full Scale Fits

Using the method described in the last section, one can obtain the flow velocities for the whole data set. This can be seen in figure 3–12. Some fits in figure 3–12(e) were omitted due to problems in the automated fitting procedure, which weren't worth fixing. The times with no data represent the fact that the measurement was in homodyne mode, so that no flow velocity could be measured. Consequently, the segment in time with no flow data is the second homodyne measurement, and lasts about 420 seconds. The other two segments represent



Figure 3–11: Time dependent flow angle for measurement 60% \uparrow heterodyne 3 heterodyne modes 2 and 3, from left to right. This same explanation carries on for the next two figures in this section.

The same fit for the flow angle parameter can be seen in figure 3–13. This is an interesting result. The curve suggests that the flow does not change appreciably in direction in time. This would agree with a stable flow pattern. To supplement the data, the strain gauge data for the same measurements and times are included in figure 3–14. One can see that the flow measurements agree with the strain gauge data. As the strain rate of change slows down, so does the flow. This makes sense as the flow is a response to the strain. Another thing to note is that the smaller bumps in the flow data are not visible in the strain gauge data. This suggests that these bumps are related to a local phenomenon.



Figure 3–12: A map of the flow velocity for the whole rubber set for each stretch.



Figure 3–13: Map of the flow angle for the whole rubber data set.



Figure 3–14: The strain gauge data for the same measurements.
Another interesting feature to notice is the large bumps in the strain gauge data. They occur during the switching of modes (from homodyne to heterodyne or vice versa). This is also noticed in the flow curves which suggests this is a real phenomenon and not a glitch in the strain gauge reading. One possible explanation is that it may be due to the change in intensity of the xray beam on the sample from the switching of modes. This result is out of the scope of this thesis and will not be discussed, but should be taken into consideration in future experiments.

3.6 Supplemental: Homodyne Fits

Looking closely at the formula for the heterodyne g_1 , there is also a shear term. Unfortunately, the shear term is a bit difficult to observe due to a combination of factors. One of them is the fact that the time-dependence of the function added by the velocity term would not allow for averaging over a large time window, leading to noisier data. On the other hand, looking at the homodyne data, much less of this time dependence is observed. This makes it much easier to extract the shear.

This is seen by observing the dependence of the homodyne g_2 function on the direction of the scattering \vec{q} vector. A way to see this is to plot for bins of the same average \vec{q} value but different ϕ values one on top of the other (after normalizing). Such a figure can be seen in figure 3–15. Clearly, as ϕ changes, the g_2 function also changes. To recap, the g_2 homodyne correlation function looks as follows:

$$g_2(q,\phi,t) = 1 + \beta e^{-2\frac{t}{\tau_d}} \operatorname{sinc}^2(\omega_s \cos(\alpha_s)t) \operatorname{sinc}^2(\omega_s \sin(\alpha_s)t).$$
(3.16)



Figure 3–15: This is an example of a g_2 while varying ϕ for q-ring 12. The color bar on the right indicates to which ϕ each color belongs to.

It turns out that upon initial analysis, the system is not undergoing exactly diffusion. A paper from Cipelletti discussing the non-diffusive slow dynamics of soft matter systems finds that a more appropriate approximation is that of a compressed exponential [19]. The equation was then modified to:

$$g_2(q,\phi,t) = 1 + \beta e^{-2\left(\frac{t}{\tau_d}\right)^{\mu}} \operatorname{sinc}^2(\omega_s \cos(\alpha_s)t) \operatorname{sinc}^2(\omega_s \sin(\alpha_s)t), \qquad (3.17)$$

where $\mu = 2$ is taken. The importance of this analysis is to extract the ϕ dependence of the g₂ correlation function, and the approximation does not change the results.

For these data, plotting the g_2 functions as a color contour plot would give easier comparison. An example of such a figure can be seen in figure 3–16. As ϕ changes for constant q, the homodyne correlation function changes.



Figure 3–16: Here is an example of a g_2 image for q-ring 12. The g_2 functions are being plotted side by side. The color indicates height. Regions of the same color indicate the g_2 functions have the same value at those points. A frame is 2.1 seconds here.

Equation 3.16 is used to fit the data in figure 3–16. Figure 3–17 compares data to theory. Observing by eye, it is clear that the trends agree well. The shear parameter is around $3\frac{\dot{A}}{s}$, with an angle close to the flow angle for this data set. After the ϕ dependence is extracted, the original g₂ functions are re-plotted for stretch 20% \uparrow 2 homodyne 2 as shown in figure 3–18. The extraction of the ϕ dependence involves dividing the g₂ function by the ϕ dependent function fitted to. The compressed exponential term $(e^{-(\frac{2t}{\tau})^{\mu}})$ from equation 3.17 is ignored. What this then shows is the ϕ independent decay term, regardless of the initial fit guess of the compressed exponential term.

A comparison of the fits for q values 5 through 12 can be seen in figure 3–19, showing the efficacy of this simple shear theory. The parameter β in equation 3.17 was also allowed to vary for each bin slightly (about 10%), due to the low number



Figure 3–17: Comparison of some measured g_2 's versus fitted g_2 's.



Figure 3–18: A plot of the g_2 functions on top of each other for q-ring 18, with the fitted shear term divided out. The color bar on the right indicates the corresponding ϕ for each g_2 .



Figure 3–19: A plot of the original g_2 and it's shear-extracted version plotted sideby-side in sequence from q-ring 5 to 12. The horizontal axis is the time delay τ . The color scale indicates the angle for the respective q-ring. It is clear in these figures that the decay is not a simple exponential in t. The decay time also decreases for high q.

of speckles averaged over, as was explained in chapter 2. What is interesting here is that only a few parameters, τ_d , α_s , γ and β were used to fit gigabytes of data². The results show that the ϕ dependence is adequately removed by use of these parameters, and allows the examination of this ϕ independent decay term. From the plots in figures 3–18 and 3–19, it is clear that the decay is not exponential. One indicator is the fact that the slope of the function is zero at zero time. Not only is the flow velocity gradient well described with this theory, it paves the path for further analysis into the random component of the data. This is rather powerful, as it has allowed for the filtering of gigabytes of data into two distinct phenomena: flow and randomness.

On the flow side, these data show that there's a difference of $3\frac{A}{s}$ from the center of the scattering volume to the edges. The velocity for this stretch (20% \uparrow homodyne 2) can be inferred from the following heterodyne measurement. The velocities for these different stretches ranged from close to zero to near $80\frac{A}{s}$. A shear velocity gradient of $3\frac{A}{s}$ is comparable in size to the flow velocity and shows that it is important for the measurements.

² Again, β was allowed to vary due to the fact of the low number of speckles sampled. Its value varies in a random manner, fluctuating near 10% of its mean value for each q ring as expected.



Figure 3–20: Contour lines of hyperbolic flow

For the randomness, the data demonstrate that the randomness is isotropic (not ϕ dependent). Furthermore, it cannot be simple diffusion, which is represented by a simple exponential in equation 3.16 but rather a compressed exponential as in equation 3.17. This is an interesting conclusion signifying that the physics of the random motion of these materials needs to be revisited.

The data results now give enough information as to guess a location where the scattering volume is, with respect to the nominal center of the flow pattern. One would expect hyperbolic flow from the measurements, and a schematic representation of such flow is given in figure 3–20. Figure 3–21 shows an example of the simple shear with the flow pointing along the x-axis of the graph and the shear velocity pointing the same direction, along the y-axis. The flow measured points on average at 260°. This suggests that for a hyperbolic flow, the scattering volume



Figure 3–21: A sample flow pattern for flow and shear in the x-direction.

must be in the upper right quadrant or the lower left quadrant of the sample, closer to the horizontal axis, according to figure 3–20. This is in accordance with the measurements, which estimate that the scattering volume was close to the center of the sample.

Another interesting thing is that the random motion is better approximated by a compressed exponential, as mentioned in the earlier section. This means that the sample is not undergoing conventional diffusion. This is interesting in the respect that it is believed that samples such as this involve random processes called jamming [20]. The time scale of this process is longer than the time scales analysed here. It would be interesting to continue measurements on systems such as these for longer time scales.

CHAPTER 4 Analysis and Conclusion

The dynamics of an ethylene-propylene cross-linked polymer were analyzed through xray scattering from a partially coherent beam. Xray scattering was chosen due to the opaque nature of the sample, and the small length scales at which the dynamics occur. Two techniques were demonstrated. One, homodyne XIFS, measured the coherent scattering from the sample to study the intensityintensity correlation function. The other, heterodyne XIFS, probed the electric field correlation function. The homodyne XIFS allowed for the measurement of the velocity gradient, as well as the diffusive nature of the elastomer. The heterodyne XIFS allowed for the measurement of a uniform velocity. The analysis of the two techniques worked on here opens two interesting branches of study: the measurement of flow patterns and the random behaviour of soft matter systems with strong dynamics.

The homodyne and heterodyne data were both necessary in order to measure the flow patterns. The uniform flow velocity was extracted from the heterodyne data. It was necessary to modify the analysis of the data in order to be able to use a time-independent theory to measure time-dependent flow velocities. Fit results of the velocity showed it to have a strong time-dependent nature, as expected. It also changed in the same manner as the stress-strain curve. Fit results of the flow angle showed it to stay constant, near the same angle, implying a constant flow pattern. The homodyne data provided information on the velocity gradient. Fit results of the shear velocity showed it to vary the flow velocity an appreciable amount over the window observed. They also showed that the type of shear occurring is simple shear.

What is interesting here is that the analysis showed that the measurements and analysis can obtain information about flow velocities. Furthermore, it also showed that the analysis can extract the time dependence of these velocities. This opens up the possibility of a wide range of experiments involving measuring the flow velocity of fluids, as well as their gradients. These experiments can even involve the most opaque of fluids, unlike traditional light scattering experiments. One possible experiment, which will be the focus of my PhD studies, is the measurement of flow velocities along boundary walls. Currently, the boundary conditions of the flow velocity along channels is still not known. This technique would provide a method of addressing this question. The information of these boundary conditions becomes more important as the effective size of the channels where the fluids flow gets smaller and smaller. This is especially important in nanofluidic devices, which are widely used in biochemistry[21].

There is another interesting branch of study that these techniques pave the way to. It is the analysis of the random motion in these types of systems. Further analysis of the homodyne data demonstrated that the flow velocity profile of the system can be separated from the random diffusive nature of the elastomer. This necessitated a good understanding of the type of velocity gradient observed, and to what order it contributed to the overall correlation function. With the gradient understood, a simple division of its contribution to the homodyne correlation function from the data allowed for the probing into another important phenomenon: the randomness of the particles in the elastomer. The random motion was shown to be isotropic and dependent upon a time scale longer than that of the velocity gradient (shear). Further analysis of the data on longer time scales will help to better understand the phenomenon.

This is interesting in the respect that the random dynamics of soft matter systems are still not well understood. Evidence suggests that these systems undergo what is called "non-diffusive behaviour" [19]. This term is characterized by a deviation from usual Brownian motion of particles. Such deviations can occur in densely packed systems where the motion of particles are partially impeded by their neighbors. An example of this is jamming, where, as the particles diffuse, they get into configurations that keep them from moving further ([20], [22]). Such an idea can be seen for example, in arched bridges made of bricks, where the bricks at the center of the bridge are kept from falling due to the fact that they are "locked" by the surrounding bricks. These "locked" configurations can persist over time scales longer than the diffusion time and can be observed by the longer range order in time of the correlation function. Currently, these dynamics are not well understood and under active study. Two examples can be seen in references [23], and [24], where the shape of the intensity-intensity correlation function is examined for colloidal particles. Another example can be seen in reference [25], where jamming is observed through the examination of stress-strain experiments.

This behaviour can be observed by the examination of the intensity-intensity correlation functions from coherent radiation. What generally happens is that the correlation function no longer has a simple exponential decay shape, but rather, a "compressed exponential" [19]. In the measurements here, this is what is observed, as was seen in the last chapter. The separation of the correlation function into a part due to shear velocity gradients and another part due to the random motion helped better observe this phenomenon. Although the system was not measured over enough time to determine what kind of random motion is occurring, the evidence remains conclusive that the elastomer is not undergoing regular Brownian motion. These are exciting results which pave a way to further study and better understanding these materials.

This analysis successfully demonstrated that it can be applied to two distinct and important branches of study: flow patterns and random behaviour of particles in viscoelastic materials. Both branches are equally powerful in their own right. As was seen, they open the possibility of a new set of experiments to be done to help further understand the inner workings of materials. As xray synchrotron sources are becoming more and more coherent, these results will become easier and easier to measure.

APPENDIX A Shear Velocity

Figure A–1 demonstrates simple shear. The shear velocity points in the y direction. The velocity increases linearly as x increases.

The shear velocity is then:

$$\vec{v}(x) = \gamma x \hat{y},\tag{A.1}$$

where γ is some arbitrary constant. This shear velocity can then be represented as the following matrix:

$$\overleftrightarrow{\Gamma} = \gamma \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$
 (A.2)

Suppressing the matrix notation for simplicity, this leaves the shear velocity to be:

$$V = \Gamma X, \tag{A.3}$$

where V is the velocity, X is the position and Γ is the shear tensor.

Now, the shear velocity does not necessarily point in the \hat{y} direction in the experiments. A rotation of the coordinate axes must be permitted. This rotation can be seen in figure A–2 and is represented by a rotation matrix¹.

 $^{^{1}}$ Note that the axes have been relabeled. The non-prime coordinate system is the laboratory coordinate system



Figure A–1: Figure of simple shear.



Figure A–2: Representation of simple shear along a plane which has an angle α_s with respect to the x axis.

To change to this new reference frame, the following transformations are made (again suppressing matrix notation):

$$X' = RX \tag{A.4}$$

$$V' = RV, \tag{A.5}$$

where:

$$R = \begin{bmatrix} \cos \alpha_s & \sin \alpha_s & 0 \\ -\sin \alpha_s & \cos \alpha_s & 0 \\ 0 & 0 & 1 \end{bmatrix}$$
(A.6)

This brings the shear equation to be:

$$V' = \Gamma' X' \tag{A.7}$$

$$RV = \Gamma' RX \tag{A.8}$$

$$V = R^{-1} \Gamma' R X, \tag{A.9}$$

where now:

$$\Gamma = R^{-1} \Gamma' R$$
(A.10)

$$\Gamma = \begin{bmatrix} -\cos \alpha_s \sin \alpha_s & -\sin^2 \alpha_s & 0 \\ \cos^2 \alpha_s & \cos \alpha_s \sin \alpha_s & 0 \\ 0 & 0 & 0 \end{bmatrix}$$
(A.11)

One can see this is correct by examining the simple cases when α_s is 0, $\frac{\pi}{2}$ etc. A plot for $\alpha_s = 25^{\circ}$ is shown as well, just to be convinced this is correct.



Figure A–3: Plot of the shear for 25° .

$\begin{array}{l} \textbf{APPENDIX B} \\ \textbf{The} \ g_1 \ \textbf{function} \end{array}$

For a particle undergoing diffusion with an average velocity $\vec{V} = \vec{U} + \overleftarrow{\Gamma} \cdot \vec{r}$, a paper by G.G. Fuller[15], gives g_1 to be:

$$g_1(\vec{q},t) = e^{-\{\int_0^t [Dq'^2(t') + i\vec{U} \cdot \vec{q'}(t')dt'\}} \int \int \int d^3x I(\vec{x}) e^{-i\int_0^t dt' \vec{q'}(t') \cdot \overleftarrow{\Gamma} \cdot \vec{x}}$$
(B.1)

$$\frac{d\vec{q'}}{dt} = -\Gamma^T \cdot \vec{q'}, \quad \vec{q'}(0) = \vec{q}$$
(B.2)

where D is the diffusion constant, $\overleftarrow{\Gamma}$ is the shear velocity gradient and $I(\vec{x})$ is the intensity of the incoming beam. So to get the heterodyne correlation function, the following must be solved:

$$\frac{d\vec{q'}}{dt} = -\overleftarrow{\Gamma}^T \cdot \vec{q'}$$
(B.3)
$$= \gamma \begin{bmatrix} \cos \alpha_s \sin \alpha_s & -\cos^2 \alpha_s & 0\\ \sin^2 \alpha_s & -\cos \alpha_s \sin \alpha_s & 0\\ 0 & 0 & 0 \end{bmatrix} \cdot \vec{q'}$$
(B.4)

which yields:

$$\frac{dq'_x}{dt} = \gamma(\cos\alpha_s \sin\alpha_s q'_x - \cos^2\alpha_s q'_y) \tag{B.5}$$

$$\frac{dq'_y}{dt} = \gamma(\sin^2 \alpha_s q'_x - \sin \alpha_s \cos \alpha_s q'_y)$$
(B.6)

$$\frac{dq'_z}{dt} = 0 \tag{B.7}$$

with:

$$\vec{q'}(0) = (q_x, q_y, q_z)$$
 (B.8)

By noticing that:

$$\frac{dq'_x}{dt}(\tan\alpha_s) = \frac{dq'_y}{dt} \tag{B.9}$$

And taking the derivative with respect to time of equations B.5 and B.6, substituting in B.9, it follows that:

$$\frac{d^2 q'_x(t)}{dt^2} = 0 (B.10)$$

$$\frac{d^2 q'_y(t)}{dt^2} = 0 (B.11)$$

This means that:

$$q'_x = C_{1x}t + q_x \tag{B.12}$$

$$q'_y = C_{1y}t + q_y$$
 (B.13)

$$q_z' = q_z \tag{B.14}$$

by substituting eq B.12 into the eq B.5 and eq B.9, two equations with two unknowns are obtained:

$$C_{1x}(\tan \alpha_s) = C_{1y} \tag{B.15}$$

$$C_{1x} = \gamma(\cos \alpha_s \sin \alpha_s (C_{1x}t + q_x) - \cos^2 \alpha_s (C_{1y}t + q_y))$$
 (B.16)

Substituting eq B.15 into eq B.16 yields a simple equation (time dependence cancels as should be expected):

$$C_{1x} = \gamma(\cos\alpha_s \sin\alpha_s q_x - \cos^2\alpha_s q_y) \tag{B.17}$$

$$= q\gamma\cos\alpha_s\sin(\alpha_s - \phi) \tag{B.18}$$

Carrying out the same procedure for y produces a similar result:

$$C_{1y} = \gamma(\sin^2 \alpha_s q_x - \cos \alpha_s \sin \alpha_s q_y) \tag{B.19}$$

$$= q\gamma \sin \alpha_s \sin(\alpha_s - \phi) \tag{B.20}$$

(Where the simplification $q_x = q \cos \phi$ and $q_y = \sin \phi$ has been made) Finally, the solution looks as follows:

$$\vec{q'} = \vec{q_s}\gamma t + \vec{q} \tag{B.21}$$

where

$$\vec{q_s} = q \begin{bmatrix} \cos \alpha_s \sin(\alpha_s - \phi) \\ \sin \alpha_s \sin(\alpha_s - \phi) \\ 0 \end{bmatrix}$$
(B.22)
$$\vec{q} = \begin{bmatrix} q_x \\ q_y \\ q_z \end{bmatrix}$$
(B.23)

To solve the space integral of eq 2.8 it is necessary to calculate:

$$\int_0^t dt' \vec{q'}(t') \cdot \overleftarrow{\Gamma} \cdot \vec{x} = \int_0^t dt' (\vec{q_s} \gamma t + \vec{q}) \cdot \overleftarrow{\Gamma} \cdot \vec{x}$$
(B.24)

On calculating the first term:

$$\begin{split} \vec{q_s}\gamma t \cdot \vec{\Gamma} \cdot \vec{x} &= q\gamma t \begin{bmatrix} \cos\alpha_s \sin(\alpha_s - \phi) \\ \sin\alpha_s \sin(\alpha_s - \phi) \\ 0 \end{bmatrix}^T \\ &\cdot \gamma \begin{bmatrix} -\cos\alpha_s \sin\alpha_s & -\sin^2\alpha_s & 0 \\ \cos^2\alpha_s & \cos\alpha_s \sin\alpha_s & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} \\ &= q\gamma^2 t \begin{bmatrix} \cos\alpha_s \sin(\alpha_s - \phi) \\ \sin\alpha_s \sin(\alpha_s - \phi) \\ 0 \end{bmatrix}^T \cdot \begin{bmatrix} -\cos\alpha_s \sin\alpha_s x - \sin^2\alpha_s y \\ \cos^2\alpha_s x + \cos\alpha_s \sin\alpha_s y \\ 0 \end{bmatrix} \\ &= q\gamma^2 t [(\cos\alpha_s \sin(\alpha_s - \phi))(-\cos\alpha_s \sin\alpha_s x - \sin^2\alpha_s y) \\ &+ (\cos\alpha_s \sin(\alpha_s - \phi))(\cos\alpha_s \sin\alpha_s x + \sin^2\alpha_s y)] \\ &= 0 \end{split}$$

By refactoring the expression, it is clear that it yields zero. Calculating the second term gives:

$$\vec{q} \cdot \overleftarrow{\Gamma} \cdot \vec{x} = q \begin{bmatrix} \cos \phi \\ \sin \phi \\ 0 \end{bmatrix}^{T} \cdot \gamma \begin{bmatrix} -\cos \alpha_{s} \sin \alpha_{s} & -\sin^{2} \alpha_{s} & 0 \\ \cos^{2} \alpha_{s} & \sin \alpha_{s} \cos \alpha_{s} & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (B.25)$$

$$= q \gamma \begin{bmatrix} \cos \phi \\ \sin \phi \\ 0 \end{bmatrix}^{T} \cdot \begin{bmatrix} -\cos \alpha_{s} \sin \alpha_{s} x - \sin^{2} \alpha_{s} y \\ \cos^{2} \alpha_{s} x + \sin \alpha_{s} \cos \alpha_{s} y \\ 0 \end{bmatrix} \quad (B.26)$$

$$= q \gamma [-\cos \phi \cos \alpha_{s} \sin \alpha_{s} x - \cos \phi \sin^{2} \alpha_{s} y \\ +\sin \phi \cos^{2} \alpha_{s} x + \sin \phi \sin \alpha_{s} \cos \alpha_{s} y] \quad (B.27)$$

$$= q\gamma\sin(\phi - \alpha_s)(x\cos\alpha_s + y\sin\alpha_s)$$
(B.28)

$$= q\gamma \vec{r} \cdot \hat{n_{\perp}} \cos(\phi - \alpha_s) \tag{B.29}$$

$$= q |\vec{v_s}| \sin(\phi - \alpha_s) \tag{B.30}$$

$$= \vec{q} \cdot \vec{v_s} \tag{B.31}$$

Where $\vec{v_s}$ is the shear velocity and $\frac{\pi}{2} + \alpha_s - \phi$ is the angle between \vec{q} and $\vec{v_s}$ (see figure). (The last few steps were just to verify that eq B.28 leads to the correct result). Solving for eq B.24:

$$\int_0^t dt' \vec{q'}(t') \cdot \overleftarrow{\Gamma} \cdot \vec{x} = \int_0^t dt' q\gamma \sin(\phi - \alpha_s) (x \cos \alpha_s + y \sin \alpha_s) \quad (B.32)$$

$$= q\gamma t \sin(\phi - \alpha_s)(x \cos \alpha_s + y \sin \alpha_s)$$
 (B.33)

The spatial integral in eq B.33 is then:

$$\int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \int_{-\frac{d}{2}}^{\frac{d}{2}} dx dy dz I e^{-i(q\gamma t \sin(\phi - \alpha_s)(x \cos \alpha_s + y \sin \alpha_s))}$$
(B.34)

$$= I da^2 \operatorname{sinc}(\omega_s t \sin \alpha_s) \operatorname{sinc}(\omega_s t \cos \alpha_s)$$
(B.35)

$$\omega_s = q\gamma \frac{a}{2}\sin(\phi - \alpha_s) \tag{B.36}$$

Where a top-hat shape was assumed for the intensity I (constant intensity in the volume considered and that the volume integrated on is a square with sides a and depth d) The full heterodyne scattering function is then:

$$G_1(\vec{q},t) = e^{-\int_0^t [Dq'^2(t') + i\vec{U} \cdot \vec{q'}(t')]dt'} Ida^2 \operatorname{sinc}(\omega_s t \sin \alpha_s) \operatorname{sinc}(\omega_s t \cos \alpha_s)$$
(B.37)

$$\frac{d\vec{q'}}{dt} = -\Gamma^T \cdot \vec{q'}, \vec{q'}(0) = \vec{q}$$
(B.38)

Now what is the $\vec{U} \cdot \vec{q}$ term?

$$\vec{U} \cdot \vec{q'} = \vec{U} \cdot (\vec{q_s}\gamma t + \vec{q}) \tag{B.39}$$

$$= U \begin{vmatrix} \cos \alpha_f \\ \sin \alpha_f \\ 0 \end{vmatrix} \cdot \begin{vmatrix} \gamma t \\ \gamma t \end{vmatrix} \begin{vmatrix} -\sin \alpha_s \cos(\phi - \alpha_s) \\ \cos \alpha_s \cos(\phi - \alpha_s) \\ 0 \end{vmatrix} + \vec{q}$$
(B.40)

$$= Uq[\gamma t \sin(\alpha_f - \alpha_s) \cos(\phi - \alpha_s) + \cos(\alpha_f - \phi)]$$
(B.41)

This then gives:

$$-i\int_{0}^{t} dt' \vec{U} \cdot \vec{q'} = -i\int_{0}^{t} dt' Uq[\gamma t \sin(\alpha_f - \alpha_s)\cos(\phi - \alpha_s) + \cos(\alpha_f - \phi)]B.42)$$
$$= -iqUt[\gamma \frac{t}{2}\sin(\alpha_f - \alpha_s)\cos(\phi - \alpha_s) + \cos(\alpha_f - \phi)] \quad (B.43)$$

Assuming the shear is negligible:

$$q'^{2} = \vec{q'} \cdot \vec{q'} = q_{s}^{2} \gamma^{2} t^{2} + \gamma t \vec{q_{s}} \cdot \vec{q} + q^{2}$$
(B.44)

$$= q^2 + \mathcal{O}(\gamma t) \tag{B.45}$$

The diffusion term in the scattering function is just:

$$\int_0^t Dq^2 dt' = Dq^2 t \tag{B.46}$$

This then leaves the whole g_1 function to look like $(g_1(\tau) = \frac{G_1(\tau)}{G_1(0)})$:

$$g_1(\vec{q}, t) = e^{-\frac{t}{\tau}} e^{iqUtA(\alpha_f, \alpha_s, \phi, t)} \operatorname{sinc}(\omega_s t \sin \alpha_s) \operatorname{sinc}(\omega_s t \cos \alpha_s)$$
(B.47)

$$A(\alpha_f, \alpha_s, \phi, t) = \left[\gamma \frac{t}{2} \sin(\alpha_f - \alpha_s) \cos(\phi - \alpha_s) + \cos(\alpha_f - \phi)\right]$$
(B.48)

$$\omega_s = q\gamma \frac{a}{2}\sin(\phi - \alpha_s) \tag{B.49}$$

$$\tau = (Dq^2)^{-1}.$$
 (B.50)

In general, the effect of the shear is negligible compared to the effect of the flow velocity, so A can be approximated to be:

$$A(\alpha_f, \alpha_s, \phi, t) \approx \cos(\alpha_f - \phi). \tag{B.51}$$

This gives the g_1 correlation function to be:

$$g_1(\vec{q},t) = e^{-\frac{t}{\tau}} e^{iqUt\cos(\alpha_f - \phi)} \operatorname{sinc}(\omega_s t \sin \alpha_s) \operatorname{sinc}(\omega_s t \cos \alpha_s)$$
(B.52)

APPENDIX C Rubber Information

The type of material measured was ethylene-propylene rubber (EPR, Buna AP 301). This is a synthetic material and was created in a lab under controlled conditions. The filler used for the rubber was carbon black N330 (Sid Richardson). The cross-linking agent is dicumyl peroxide [26]. The rubber was stretched at different intervals. Here is a table of describing the measurements of the elastomer:

Stretch $\#$	% Elongation	Name
1	0%	0%
2	20%	$20\% \uparrow 1$
3	40%	$40\% \uparrow 1$
4	60%	$60\% \uparrow 1$
5	40%	$40\% \downarrow 1$
6	20%	$20\% \downarrow 1$
7	0%	$0\% \downarrow 1$
8	20%	$20\% \uparrow 2$
9	40%	$40\% \uparrow 2$
10	60%	$60\% \uparrow 2$

Table C–1: A list of the elongations per stretch number

Frames	Type	Time Per Frame
1 - 100	Heterodyne 1	2.5s
100 - 110	Dark	2.5s
111 -210	Homodyne 1	2.1s
211 - 220	Dark	2.1s
221 - 420	Heterodyne 2	2.5s
421 - 430	Dark	2.5s
431 - 630	Homodyne 2	2.1s
631 - 640	Dark	2.1s
641 - 1140	Heterodyne 3	2.5s
1141 - 1150	Dark	2.5s
1151 - 1650	Homodyne 3	2.1s
1651 - 1660	Dark	2.1s

Table C–2: Measurement types for each frame in a stretch

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