Nuclear resonance time domain interferometry (NR-TDI) is used to study the slow dynamics of liquids (that do not require Mössbauer isotopes) at atomic and molecular length scales between 1 Å to 10 nm and at time scales between 1 ns to 10 µs. This new spectroscopy technique covers a new range of previously unexplored momentum transfers between 1 to 100 nm$^{-1}$ and energies between 10 peV to 100 neV allowing an investigation into the dynamical motion of molecules, liquids, and glasses. The notoriously low count rate from quasielastic scattering experiments makes measurements difficult when using synchrotron x-rays or radioactive sources. The introduction of an annular slit allowed the entire diffraction ring to be measured, instead of only a fraction of the ring, increasing the count rate by two orders of magnitude at the peak of the structure factor of glycerol. The fabrication of the annular slits increased the count rate sufficiently that it allowed for measurements at different momentum transfers with low scattering intensities. These measurements can give new insights into the dynamics of the liquids improving the understanding about their behavior under different conditions of temperature, pressure, and length scales. The intermediate scattering function describes the motion of molecules in liquids under different temperatures and
momentum transfers using the Kohlrausch–Williams–Watts (KWW) stretch exponential as a model. The relaxation times from the KWW model gives insight into the dynamics of the electron density fluctuations of glycerol. I was able to measure relaxation times from 5 to 70,000 ns. The Vogel–Fulcher–Tammann (VFT) equation was used to determine the glass transition \( T_g = 185 \text{ K} \) of glycerol, and the Arrhenius equation was used to find its activation energy \( E_a = 63 \text{ kJ mol}^{-1} \). With the addition of an annular slit, NR-TDI experiments can be easily implemented at any beamline using a single detector, eliminating the need for multiple detectors. The increase in count rate using an annular slit makes it possible to do material science experiments on various liquid systems like glycerol, liquid crystals, proteins, colloids, and biomolecules.
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As a dyslexic person who never thought they would have an opportunity to become a PhD physicist,

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DEDICATION

I dedicate my thesis to my wife Tara for believing in me and giving me the opportunity to live my dream. I also dedicate my thesis to my children Sydney, Austin, and Casey, and my late parents Rosemarie and Andrew.
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CHAPTER 1
INTRODUCTION TO NR-TDI

There are many different spectroscopy techniques covering a wide range of time and length scales, as shown in Figure 1.1. Nuclear resonance time domain interferometry (NR-TDI) covers an unexplored range of momentum transfers between 1 to 100 \text{nm}^{-1} (or length scales between 1 Å to 10 nm) and energies approximately between 10 \text{peV} to 100 \text{neV} (or time scales between 1 \text{ns} to 10 \text{µs}).[1] This new technique enables a deeper investigation of the dynamical motion of molecules, liquids, and glasses.

Starting back in the early 1960s before the advent of time domain interferometry measurements, various Mössbauer measurements were done in an attempt to explore relaxation dynamics. Initial measurements studied the diffusion of $^{57}\text{Co}$ or $^{57}\text{Fe}$ ions embedded in glycerol.[2, 3] These early conventional transmission Mössbauer experiments studied how the motion of the ions caused diffusional broadening of the linewidths. Later, Mössbauer Rayleigh scattering experiments on $^{57}\text{Fe}$ ions embedded in glycerol were performed.[4] For these quasielastic scattering experiments, the diffusional broadening of the linewidths could be measured as a function of both temperature and momentum transfer. Eventually researchers realized that this scattering technique can be used to examine the motion of the individual glycerol molecules. Champeney et al. used Mössbauer Rayleigh scattering to investigate the molecular motions of supercooled liquids (without embedded Fe ions) by relating how the linewidth broadening is caused by molecular diffusion and viscosity using the Stokes–Einstein equation.[5] The disadvantage with these Rayleigh scattering techniques were the extremely low counting rates and, thus measurements can take up to several weeks.
Figure 1.1: Experimental techniques that measure the dynamics of materials and the time and length scales they cover.

The first-time domain interferometer experiment using synchrotron x-rays to measure the relaxation times of glycerol was performed at the European Synchrotron Radiation Facility (ESRF).[6] This technique involved a moving $^{57}$Fe enriched stainless-steel foil (called a single line source) attached to a constant velocity drive, a liquid sample, and a stationary enriched
stainless-steel foil (called a single line analyzer) in front of an avalanche photodiode (APD) detector. Baron et al. did measurements as a function of temperature, but at only a single momentum transfer. Typical counting rates from this source/analyzer setup were around 2 Hz. This technique was improved by using a multielement detector array having eight APD detectors to measure four different scattering angles simultaneously at the ESRF beamline ID-22N.[7] This arrangement, for a particular scattering angle, allowed Smirnov et al. to basically increase the counting rate by a factor of two (two detectors were used to measure each angle). At the Spring-8 beamline BL09XU, this technique was modified by using a moving double line source rather than a moving single line source.[8] Saito et al. later extended his method using multiline moving sources and analyzers finding that this method increases the TDI efficiency.[9] Rather than using moving sources and analyzers, the technique was simplified by fixing them to be stationary. At the ESRF beamline ID18, TDI measurements were done using a stationary double line source and single line analyzer.[10] The stationary double line source consisted of a magnetized $^{57}$Fe foil, with the field perpendicular to both the direction of the beam and the incident electric field polarization. These experiments have slightly different setups but all suffer from low counting rates. We were able to improve the counting rates by a factor of two orders of magnitude using an annular slit. Using a similar setup as Caporaletti et al., and placing the annular slit on the downstream single APD detector, we have been able to make practical measurements, even at low momentum transfers, which has not been achievable before.

Spectroscopy is the science of measuring wavelengths of atomic, molecular, and nuclear emissions. There are many ways of measuring wavelengths of atoms and molecules, one being an interferometer. The first interferometer was invented by an American physicist Albert A. Michelson winning him a Nobel Prize in 1907[11]. It splits a beam of light into two paths and then recombines them to form an interference pattern. It has been used for over a century to make precise measurements of wavelengths and distances. In 1887 with
the help of Edward W. Morley, the famous Michelson-Morley null experiment was trying to show the velocity of earth relative to the mysterious ether. They expected to see a change in the interference pattern when rotating the interferometer by 90° because the velocity of the light would add differently with the velocity of the ether when rotated, instead they saw no significant change in the interference pattern[12]. It was not until Albert Einstein’s postulates for his special theory of relativity stating that the speed of light in vacuum is constant in all inertial frames[13]. This explains why Michelson-Morley showed no change in the velocity of the light regardless of the fictitious ether drift direction because the speed of light is constant in all reference frames.

![Michelson-Morley interferometer](image)

Figure 1.2: A Michelson-Morley interferometer.

The Michelson-Morley interferometer, shown in Figure 1.2, works when a source of light is split by a beam splitter, where one arm is projected onto mirror 1 and the second arm continues forward onto mirror 2. The two beams of light are then added back together to produce an interference pattern, similar to Figure 1.3(a). By adjusting the position of mirror 2, which changes the length of arm 2, the interference from arm 2 can construc-
tively or destructively interfere with arm 1 producing a new interference pattern allowing for measurements of the wavelength of light and the indices of refraction of air.

(a) Michelson-Morley interferometer spatial interference data[14]  
(b) NR-TDI time interference data

Figure 1.3: Michelson-Morley and NR-TDI interferometer patterns

In a similar manner, NR-TDI measures the interference of electric fields in time rather than space. The Michelson-Morley interferometer uses mirrors to measure inference patterns of optical light, whereas the NR-TDI uses iron foils to measure the interference patterns of x-rays. A magnetized α-^{\text{57}}Fe foil acts like arm 1 and a stainless-steel foil acts like arm 2 of the interferometer. The electric fields from the foils superimpose to produce a time domain interference pattern as shown in Figure 1.3(b). Important physical properties of a sample (such as the index of refraction) can be found by placing the sample in one of the arms of the Michelson-Morley interferometer. Similarly, we can find important physical properties of a sample (such as fluctuations in time of the index of refraction) by placing it between the arms (iron foils) of the NR-TDI interferometer. Thus, the interference patterns can be used to measure the average relaxation time of the fluctuations in the electron density of a liquid sample.
CHAPTER 2
SCATTERING THEORY AND SAMPLE DYNAMICS

2.1 Quantum Scattering Theory

The history of understanding liquids begins more than 2000 years ago with ancient Greek mathematician Archimedes defining fundamental principles of hydrostatics and dynamics.[15] In the late 15th century, Leonardo da Vinci studied the movement of liquids in small capillary tubes. In the 17th century, Isaac Newton postulated his laws of motion and the law of viscosity of the linear fluids. In early 18th century, Daniel Bernoulli published the first textbook about hydrodynamics called “Hydrodynamica” studying the motion of fluids. The 19th century British physicist, Lord Rayleigh studied elastic scattering of light explaining why the sky is blue. The understanding of the liquid dynamics on the atomic and molecular level entered a new era with the scattering of light.

The quantum theory of scattering begins with an incident plane wave

$$\psi(z) = Ae^{i(kr - \omega t)}$$

(2.1)

where \( k \) is a vector whose magnitude is \( k = \omega / c \) and is in the direction of propagation. The scattered wave consists of a plane wave and a spherical wave modified by a scattering amplitude:

$$\psi(r, \theta, \phi) \approx A \left( e^{ikz} + f(\theta, \phi) \frac{e^{ikr}}{r} \right)$$

(2.2)
where the scattering amplitude \( f(\theta, \phi) \) is the probability of scattering into the angles \( \theta \) and \( \phi \). The absolute squared of the scattering amplitude is related to the differential cross-section:[16]

\[
\frac{d\sigma}{d\Omega} = |f(\theta, \phi)|^2
\]  

(2.3)

2.1.1 The Born Approximation

In quantum mechanics the scattering can be described by the time-independent Schrödinger equation

\[
-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi \quad \text{or} \quad \hat{H} |\psi\rangle = E |\psi\rangle
\]

(2.4)

and defining \( k \equiv \sqrt{\frac{2mE}{\hbar}} \) and \( Q \equiv \frac{2m}{\hbar^2} V\psi \),[16, 17] then substituting those equations into the Schrödinger equation gives

\[
(\nabla^2 + k^2)\psi = Q
\]

(2.5)

where \( Q \) is inhomogeneous term depending on \( \psi \). Equation (2.5) is the Helmholtz equation, when \( Q = 0 \). Suppose there is a function, which will be the Green’s function \( G(r) \), that can solve the Helmholtz equation with a delta function.

\[
(\nabla^2 + k^2)G(r) = \delta^3(r)
\]

(2.6)

Assume \( \psi \) can be expressed by the integral:

\[
\psi(r) = \int G(r - r')Q(r') \, d^3r'
\]

(2.7)
Substituting this integral into the left side of Equation (2.5) to see if it satisfies the Schrödinger equation gives

\[(\nabla^2 + k^2)\psi(r) = \int (\nabla^2 + k^2)G(r - r')Q(r')\,d^3r'.\]

Using Equation (2.6) to define \((\nabla^2 + k^2)G(r - r') = \delta^3(r - r')\) and substituting it into the above equation gives

\[(\nabla^2 + k^2)\psi(r) = \int \delta^3(r - r')Q(r')\,d^3r'.\]

Using a fundamental property of a delta function of \(\int_{-\infty}^{-\infty} f(x)\delta(x - a)\,dx = f(a)\), simplifies the above expression to

\[(\nabla^2 + k^2)\psi(r) = Q(r).\]

In order to solve the Green’s function for the Helmholtz equation starts by taking the Fourier transform of some general function let’s call \(g(s)\)

\[G(r) = \frac{1}{(2\pi)^{3/2}} \int e^{i s \cdot r} g(s)\,d^3s\quad (2.8)\]

then

\[(\nabla^2 + k^2)G(r) = \frac{1}{(2\pi)^{3/2}} \int [ ( (\nabla^2 + k^2) e^{i s \cdot r} ) ] g(s)\,d^3s\]

\[= \frac{1}{(2\pi)^{3/2}} \int [ ( - s^2 + k^2 ) e^{i s \cdot r} ] g(s)\,d^3s\quad (2.9)\]
and

$$\delta^3(r) = \frac{1}{(2\pi)^3} \int e^{is \cdot r} d^3s \quad (2.10)$$

finally, the solution to the time-independent Schrödinger Equation (2.6) becomes using equations (2.9) and (2.10)

$$\frac{1}{(2\pi)^{3/2}} \int [(-s^2 + k^2) e^{is \cdot r}] g(s) d^3s = \frac{1}{(2\pi)^3} \int e^{is \cdot r} d^3s. \quad (2.11)$$

Solving for $g(s)$ gives

$$g(s) = \frac{1}{(2\pi)^{3/2}(k^2 - s^2)} \quad (2.12)$$

Substituting Equation (2.12) back into Equation (2.8) gives

$$G(r) = \frac{1}{(2\pi)^3} \int \frac{e^{is \cdot r}}{(k^2 - s^2)} d^3s.$$

Taking the dot product $s \cdot r = sr \cos \theta$

$$= \frac{1}{(2\pi)^3} \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{s^2 \sin \theta e^{is r \cos \theta}}{(k^2 - s^2)} ds d\theta d\phi$$

$$= \frac{1}{(2\pi)^2} \int_0^\pi \int_0^\infty \frac{s^2 \sin \theta e^{is r \cos \theta}}{(k^2 - s^2)} ds d\theta$$

$$= \frac{1}{4\pi^2 r} \int_{-\infty}^{\infty} \frac{s \sin [s r]}{(k^2 - s^2)} ds$$

$$= \frac{1}{4\pi^2 r} \left(-\pi e^{ikr}\right)$$

$$G(r) = -\frac{e^{ikr}}{4\pi r}. \quad (2.13)$$
Equation (2.13) is a Green’s function that satisfies the Helmholtz equation. Substituting Equation (2.13) into Equation (2.7) gives a solution to the Schrödinger equation

\[ \psi(r) = \psi_0(r) - \frac{m}{2\pi\hbar^2} \int \frac{e^{ik|r-r'|}}{|r-r'|} V(r') \psi(r') \, d^3r' \]  

(2.14)

where \( \psi_0 \) is the homogenous solution to the Schrödinger equation, \((\nabla^2 + k^2)\psi_0 = 0\).

For a typical scattering experiment, the detector is usually placed at a much larger distance away from the target compared to the size of the target. This allows for Equation (2.14) to be rewritten as using \( e^{ik|r-r'|}/|r-r'| \approx e^{ikr}/r \) because \( r \gg r' \) and it is looking at the far field region

\[ \psi(r) = Ae^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int e^{-ikr'} V(r') \psi(r') \, d^3r' \]  

(2.15)

The first order Born approximation assumes that \( V(r') \) is small perturbation, thus the scattered wave function is essentially a plane wave like the incident wave: \( \psi(r) \approx \psi_0(r) = Ae^{ikz} = Ae^{ik'z} \), where \( k' \equiv k\hat{z} \).

\[ \psi(r) = Ae^{ikz} - \frac{m}{2\pi\hbar^2} \frac{e^{ikr}}{r} \int e^{-ikr'} V(r') \left(Ae^{ik'z}\right) \, d^3r' \]  

(2.16)

Comparing Equation (2.16) to Equation (2.2) the scattering amplitude \( f(\theta, \phi) \) is then

\[ f(\theta, \phi) = -\frac{m}{2\pi\hbar^2} \int e^{i(k'-k)\cdot r'} V(r') \, d^3r' \]  

(2.17)

Figure 2.1 defines the momentum transfer as

\[ \mathbf{q} = k' - k \]  

(2.18)
where $\mathbf{k}$ is the incident wave and $\mathbf{k}'$ is the scattered wave. Using the law of cosines

\[ c^2 = a^2 + b^2 - 2ab \cos \theta \]

it can be shown that

\[ q = \frac{4\pi}{\lambda} \sin \theta \]  \hspace{1cm} (2.19)

Finally, dropping the primes because they are no longer needed, the first-order Born amplitude becomes:

\[ f(\theta, \phi) = f(q) = -\frac{m}{2\pi \hbar^2} \int e^{i\mathbf{q} \cdot \mathbf{r}} V(\mathbf{r}) d^3\mathbf{r} \]  \hspace{1cm} (2.20)

where $f(\mathbf{q})$ is the form factor.

Using Equation (2.2) (ignoring the incoming plane wave), the quasielastic scattering for a single particle located at $\mathbf{r}_i$ irradiated by a plane wave with amplitude $A$ and wavevector $\mathbf{k}$ into a detector located at position $\mathbf{R}$ can be expressed by[18]

\[ \psi_1(q) = A f_i(q) \frac{e^{-i\mathbf{k} \cdot \mathbf{r}_i} e^{-i\mathbf{k}' \cdot (\mathbf{R} - \mathbf{r}_i)}}{|\mathbf{R} - \mathbf{r}_i|}. \]  \hspace{1cm} (2.21)

Assuming that $\mathbf{R} \gg \mathbf{r}_i$ and $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ simplifies the above equation for a sample of $N$ particles as (see Figure 2.2)

\[ \psi_N(q) \approx \frac{A}{R} e^{-i\mathbf{k}' \cdot \mathbf{R}} \sum_i f_i(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i}. \]  \hspace{1cm} (2.22)
Figure 2.2: Quasielastic scattering from an incident plane wave scattered from a particle at $r_i$ in the direction $k'$.  

The scattering intensity from an $N$-particle sample is

$$I(q) = |\psi_N(q)|^2 = \frac{A^2}{R^2} \left< \sum_{i,j} f_i(q) f_j(q) e^{-iq(r_i-r_j)} \right>$$

(2.23)

where $\langle \ldots \rangle$ represents a thermodynamic ensemble average over a Maxwell-Boltzmann distribution.

Considering the self scattering term $(i = j)$

$$I_s(q) = \frac{A^2}{R^2} \left< \sum_{i=j} f_i(q) f_j(q) e^{-iq(r_i-r_j)} \right>$$

$$= \left( \frac{A \sum_i f_i(q)}{R^2} \right)^2$$

(2.24)
the static structure factor can be defined as the total intensity normalized by the self scattering intensity

\[
S(q) = \frac{I(q)}{I_s(q)} = \frac{1}{\sum_i f_i(q)^2} \left\langle \sum_{i,j} f_i(q)f_j(q)e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle
\]  

(2.25)

If all the particles are identical then the form factors are the same, \( f_i(q) = f_j(q) \), and Equation (2.25) can be rewritten as

\[
S(q) = \frac{1}{N} \left\langle \sum_{i,j} e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle.
\]  

(2.26)

Simplifying Equation (2.26) into self \((i = j)\) and distinct \((i \neq j)\) terms gives the static structure factor

\[
S(q) = 1 + \frac{1}{N} \left\langle \sum_{i \neq j} e^{-i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle.
\]  

(2.27)

The static structure factor can be related to pair correlation function by using a fundamental delta function property \( \int f(x)\delta(x-a) \, dx = f(a) \) to rewrite Equation (2.27)

\[
S(q) = 1 + \frac{1}{N} \left\langle \int_V d\mathbf{r} \, e^{-i\mathbf{q} \cdot \mathbf{r}} \sum_{i \neq j} \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] \right\rangle.
\]  

(2.28)

An alternative way of writing the summation \( \sum_{i \neq j} \delta[\mathbf{r} - (\mathbf{r}_i - \mathbf{r}_j)] = \sum_{i \neq j} \delta[\mathbf{r} - \mathbf{r}_{ij}] \) where \( \mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j \)

\[
S(q) = 1 + \frac{1}{N} \int_V d\mathbf{r} \, e^{-i\mathbf{q} \cdot \mathbf{r}} \left\langle \sum_{i \neq j} \delta[\mathbf{r} - \mathbf{r}_{ij}] \right\rangle.
\]  

(2.29)

The pair correlation function for a system of \( N \) spherically symmetric particles is[19]

\[
g(\mathbf{r}) = \frac{V}{N^2} \left\langle \sum_{i \neq j} \delta[\mathbf{r} - \mathbf{r}_{ij}] \right\rangle.
\]  

(2.30)
Substituting Equation (2.30) into Equation (2.29) shows the Fourier transformation of pair correlation function is the static structure factor

\[ S(q) = 1 + \rho \int_V dr \ e^{-iq \cdot r} g(r) \]  \hspace{1cm} (2.31)

where \( \rho = \frac{N}{V} \).

The structure factor shown above is the Fourier transform of the pair distribution function for the static case in which the particles are stationary. If the particles move over time then the pair correlation function, \( G(r, t) \), is a function of both position and time. For this case the important quantity is the intermediate scattering function, \( F(q, t) \), which is the spatial Fourier transform of the time dependent pair distribution function.

\[ F(q, t) = \int G(r, t) e^{-iq \cdot r} dr \]  \hspace{1cm} (2.32)

This time dependent pair distribution function is discussed in the next Section 2.2.

### 2.2 Dynamic Structure Factor

The dynamic structure factor is an experimental quantity describing the microscopic correlation of a system.[20] A correlation function quantifies how random microscopic variables, like electron density, can fluctuate with respect to one another in space and time. The relation between the dynamic structure factor, \( S(q, \omega) \), and the differential scattering cross section is given by Van Hove[21]

\[ \frac{d\sigma}{d\Omega} = \int \frac{d^2\sigma}{d\Omega d\epsilon} d\epsilon = \hbar A \int S(q, \omega) d\omega . \]  \hspace{1cm} (2.33)
The dynamic structure factor is the Fourier transform (in Van Hove’s notation) in time and space of the pair distribution function, \( G(\mathbf{r}, t) \):

\[
S(\mathbf{q}, \omega) = \frac{N}{2\pi} \int \exp \left[ i(\mathbf{q} \cdot \mathbf{r} - \omega t) \right] \cdot G(\mathbf{r}, t) \, d\mathbf{r} \, dt \tag{2.34}
\]

The inverse Fourier transform of \( S(\mathbf{q}, \omega) \) is given by:

\[
G(\mathbf{r}, t) = \frac{1}{(2\pi)^3} \int \exp \left[ i(\omega t - \mathbf{q} \cdot \mathbf{r}) \right] \cdot S(\mathbf{q}, \omega) \, d\mathbf{q} \, d\omega. \tag{2.35}
\]

Van Hove used the convolution formula and the Fourier transform of an ordered product to define \( G(\mathbf{r}, t) \) in terms of space and time variables:

\[
G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i,j} \int d\mathbf{r}' \, \delta[\mathbf{r} + \mathbf{r}_i(t_s) - \mathbf{r}'] \delta[\mathbf{r}' - \mathbf{r}_j(t_s + t)] \right\rangle \tag{2.36}
\]

Under classical conditions where the operators commute \(([A, B] = 0)\) Equation (2.36) can be rewritten as the Van Hove probability density function:

\[
G(\mathbf{r}, t) = \frac{1}{N} \left\langle \sum_{i,j} \delta[\mathbf{r} + \mathbf{r}_i(t_s) - \mathbf{r}_j(t_s + t)] \right\rangle \tag{2.37}
\]

The physical interpretation of the pair distribution function is that it is the average density distribution at a distance \( r \) and time \( t \) as seen from a point occupied by a particle at time \( t_s \) (called the reference point). Figure 2.3 shows the average density in a shell of thickness \( d\mathbf{r} \) containing point \( \mathbf{r}_j(t_s + t) \) (blue point) located at a distance \( r \) away from the reference point (red point).
The division into self and distinct parts corresponds to possibilities that $i$ and $j$ may be the same particle or different ones.[22] The Van Hove correlation function can be split in two terms, the self ($i = j$) and distinct ($i \neq j$) parts

$$G(r, t) = G_s(r, t) + G_d(r, t) \quad (2.38)$$

where

$$G_s(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \delta \left[ r + r_i(t_s) - r_i(t_s + t) \right] \right\rangle \quad (2.39a)$$

$$G_d(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} \sum_{j \neq i}^{N} \delta \left[ r + r_i(t_s) - r_j(t_s + t) \right] \right\rangle \quad (2.39b)$$
Notice that when \( t = 0 \) Equations (2.39a), (2.39b), and (2.38)

\[
\begin{align*}
G_s(r, 0) &= \delta(r) \quad (2.40a) \\
G_d(r, 0) &= g(r) \quad (2.40b) \\
G(r, 0) &= \delta(r) + g(r) \quad (2.40c)
\end{align*}
\]

where \( g(r) \) is the so-called pair distribution, which is also the static correlation function describing the average distance between particles in the system. As time increases \( G_s(r, t) \), the delta function in Equation (2.39a), begins to broaden into a bell-shaped curve and the oscillation of \( G_d(r, t) \), Equation (2.39b), will begin to dampen asymptotically to one. In fact, as \( t \to \infty \), both \( G_s(r, t) \) and \( G_d(r, t) \) become independent of \( r \) (the behavior at large \( r \) is the same as that at large \( t \)):

\[
\begin{align*}
G_s(r, t \to \infty) &\approx \frac{1}{V} \quad (2.41a) \\
G_d(r, t \to \infty) &\approx \rho \quad (2.41b)
\end{align*}
\]

The time-dependent, average microscopic particle density is:[22]

\[
\rho(r, t) = \left\langle \sum_{i=1}^{N} \delta[\mathbf{r} - \mathbf{r}_i(t)] \right\rangle \quad (2.42)
\]

The Van Hove probability distribution function becomes by substituting Equation (2.42) into Equation (2.36) as[22]

\[
G(r, t) = \frac{1}{t_m} \int dt_s \frac{1}{N} \int d\mathbf{r}' \rho(\mathbf{r}' - \mathbf{r}, t_s) \rho(\mathbf{r}', t_s + t) \quad (2.43)
\]
Equation (2.43) is the pair distribution function averaged over the total measurement time $t_m$. This is the density-density correlation function in real space of the microscopic motions of the atoms and molecules within a relaxation process. However, scattering experiments can only probe the microscopic dynamics in reciprocal space. The scattering intensity in measurements is proportional to the intermediate scattering function $F(q, t)$. The intermediate scattering function Equation (2.32) is the spatial Fourier transform of the pair distribution function

$$F(q, t) = \int G(r, t)e^{-iq\cdot r} \, dr$$

The dynamic structure factor is the temporal Fourier transform of the intermediate scattering function

$$S(q, \omega) = \int F(q, t)e^{i\omega t} \, dt$$

(2.44)

The stretched exponential relaxation function has been found empirically in various amorphous materials, such as glasses and liquids near the glass transition temperature. There are many phenomenological models that describe $F(q, t)$, such as the Kohlrausch–Williams–Watts (KWW) stretched exponential function. The KWW stretch exponential function is widely used to describe the relaxation processes of viscosity, friction, gas kinetics, heat transfer, and more.[23, 24]

$$F(q, t) = F(q, 0)f_q e^{-\left(\frac{t}{\tau_K}\right)^\beta} \quad \text{with } 0 < \beta < 1$$

(2.45)

where $\beta$ is the stretching coefficient, $F(q, 0)$ is the static structure factor (also called $S(q)$), $f_q$ is non-ergodicity factor, and $\tau_K$ is the relaxation time that is a function of momentum transfer $q$ and temperature $T$.[25, 26] The stretched exponential is used to describe the relaxation of glasses where molecules diffuse through the material filling traps (the “trapping model”). As the traps are filled, the remaining particles must travel longer to find unfilled traps thus
increasing the relaxation time. Were it not for these traps, $\beta$ would equal one and the system would relax with a simple exponential function.[27]

### 2.2.1 Static Structure Factor

The inverse Fourier transform of the dynamic structure factor is the intermediate scattering function:

$$F(q, t) = \frac{1}{2\pi} \int S(q, \omega) e^{i\omega t} d\omega$$

By setting $t = 0$, we get the static structure factor:

$$F(q, 0) = \frac{1}{2\pi} \int S(q, \omega) d\omega.$$  \hspace{1cm} (2.46)

The static structure factor, $F(q, t = 0) \equiv I(q)$, provides information about the average interparticle distance. It can be used to find the average intermolecular distance where $r \approx \frac{2\pi}{q_{\text{max}}}$.

Wide angle x-ray scattering (WAXS) is a tool that characterizes the structure of solids, liquids, and gases at length scales between 0.1 and 1 nm. Glycerol molecules have a size of about $(0.48 \times 0.51 \times 0.78)$nm[28], and thus have a length scale that lies within the range for WAXS measurements. Small angle x-ray scattering (SAXS) measures samples having a length scale between 1 and 100 nm, but SAXS is primarily used for samples having short-range order.

X-ray diffraction (XRD) measures samples having a length scale similar of that of WAXS, but the samples for XRD are generally crystalline materials having long-range order as shown in Figure 2.4(a). For WAXS measurements the samples are less ordered, but not completely
Figure 2.4: Two x-ray beams with the same wavelength and phase scattering off a liquid. Beam #2 traverses an extra length of $2d \sin \theta$. Constructive interference occurs at multiple integers of the wavelength.

random as seen in Figure 2.4(b). My thesis examines liquids that generally have no long-range order. However, for brief instants in time, there are quasi-crystalline islands that can have some long-range order. This gives rise to the quasi-elastic Bragg scattering peaks occurring in the WAXS $S(q)$ measurements. The values of $q$, using Bragg’s law $n \lambda = 2d \sin \theta$, are $q = \frac{2\pi}{d}$. Figure 2.5 shows both WAXS and SAXS angle ranges, momentum transfer ranges, and length scales.

Figure 2.6 shows a WAXS measurement of glycerol having a broad x-ray diffraction peak around the green circle at $q = 14.25\text{nm}^{-1}$ (or $2\theta = 11.2^\circ$). In contrast, scattering from a crystal (having long-range order) would result in sharp diffraction spots instead of the broad diffraction rings observed in scattering off liquids. The short-range order is caused by the constant motion, or diffusion, of the molecule’s average position as a function of time.

Figure 2.7 shows the one-dimensional radial integrated intensity, $I(q)$ (green curve), of the entire diffraction image shown in Figure 2.6. The red curve is the normalized intensity $S(q)$ calculated using Equation (2.25).[29] The blue curve is the form factor for
Figure 2.5: For WAXS measurements $0.1 < D < 1$ nm and for SAXS measurements $1 < d < 100$ nm. The angle and $q$ ranges for WAXS and SAXS are shown in the plot above. The green arrows are for a momentum transfer of $q = 14.25 \text{ nm}^{-1}$, which is where the structure factor for glycerol is at a maximum.

glycerol $f(q)$ calculated using Equation (2.48). For glycerol the peak occurs around $q = 14.25 \text{ nm}^{-1}$ (or $2\theta = 11.2^\circ$) determining the position of the electron density distribution and molecular spacing of the sample. The Eiger 2D detector was calibrated using CeO$_2$ as a powder diffraction standard.

The form factor is the Fourier transform of the electron density of an atom or molecule. For a spherically symmetric electron density, the Fourier transform will only depend upon the magnitude of $\mathbf{q}$ and not its direction. The atomic form factor can be approximated by a sum of Gaussians of the form

$$f(q) = \sum_{i=1}^{4} a_i \exp \left[ -b_i \left( \frac{q}{4\pi} \right)^2\right] + c$$

(2.47)
Figure 2.6: X-ray diffraction of glycerol at room temperature. The bright ring in the center corresponds to a $q = 14.25 \text{ nm}^{-1}$, represented by the green circle.

where the values of $a$, $b$, and $c$ are tabulated by Brown[30] for hydrogen, carbon, and oxygen. The molecular form factor for glycerol calculated with the independent atomic scattering approximation is[31]

$$f_{\text{Gly}}(q) = \sqrt{[3f_C(q)]^2 + [8f_H(q)]^2 + [3f_O(q)]^2}. \quad (2.48)$$

This approximation is valid at high $q$. For water the difference between the independent atomic scattering approximation and experiment starts to show below $5 \text{ nm}^{-1}$. One needs to start taking into account the geometry of the water molecule (at $5 \text{ nm}^{-1}$ the experimen-
Figure 2.7: The scattering intensity (green), static structure factor (red), and the molecular form factor (blue) for pure glycerol at room temperature.

*tal value is 3% lower). Above 6 nm\(^{-1}\), there is excellent agreement making the independent atomic scattering approximation a very good way to estimate atomic form factors for molecules.

### 2.3 NR-TDI Equation

The study of the molecular dynamics of liquids involves an understanding of relaxation times as a function of both temperature and momentum transfer. A model describing the dynamics taking into account nuclear resonance scattering from the foils and electronic scattering from the sample will be described in the next Section. The response function
used for liquids describes their molecular dynamics and can be modeled by the intermediate scattering function, $F(q, t)$, which is the Fourier transform of the Van Hove pair distribution (or electron density-density correlation) function $G(r, t)$.

### 2.3.1 Deriving the TDI Intensity Equation

The time domain interferometer measures the interference of electric fields in time rather than in space. One arm of the interferometer, called the source arm, consists of a static magnetized $\alpha^{-57}$Fe foil, and the other arm, called the analyzer arm, consists of a static stainless-steel foil. The superposition of the electric fields generated from magnetized $\alpha^{-57}$Fe and stainless-steel foils gives rise to an interference spectrum in the time domain.

![Figure 2.8: Scattering paths of the radiation through resonant $\alpha^{-57}$Fe and SS foils and non-resonant sample in the interferometer.\cite{7}] The red circles represent electronic prompt scattering, blue circles represent quasi-elastic scattering, and black circles represent nuclear resonance scattering.

The possible scattering paths for NR-TDI using two foils and a liquid sample are shown in Figure 2.8 where the red circles represent electronic prompt scattering, the blue circles represent quasi-elastic scattering, and the black circles represent nuclear resonance scattering. The first possible path (1) is solely electronic scattering (this scattering occurs promptly on the order of 100 ps). The second path (2) is nuclear resonance scattering from the $^{57}$Fe foil.
followed by quasi-elastic electronic scattering from the sample. The third path (3) is quasi-elastic electronic scattering from the sample followed by nuclear resonance scattering from the SS foil. Finally, the fourth path (4) is nuclear resonance scattering from the $^{57}$Fe foil followed by quasi-elastic electronic scattering from the sample and then followed by nuclear resonance scattering from the SS foil.

The sum of the scattered waves from a collection of atoms is given by Equation (2.22) except now $r_i$ is a function of time.[7] The response function from a liquid sample is proportional to this sum:[32]

$$g(q,t) \propto \sum_i f_i(q)e^{-iq \cdot r_i(t)}.$$ (2.49)

The probability amplitudes defined by each scattering path, shown in Figure 2.8, are given by:

$$W_1(t) = g(q,t_s)\delta(t)$$ (2.50)
$$W_2(t) = g(q,t_s + t)G_{Fe}(t)e^{-i\omega_1 t} + e^{-i\omega_2 t}$$ (2.51)
$$W_3(t) = g(q,t_s)G_{SS}(t)e^{-i\omega_3 t}$$ (2.52)
$$W_4(t) = \int_0^t dt' G_{Fe}(t - t')\left[e^{i\omega_1 (t-t')} + e^{-i\omega_2 (t-t')}\right]g(q,t_s + t')G_{SS}(t')e^{-i\omega_3 t'}.$$ (2.53)

where $G_{Fe}(t)$ and $G_{SS}(t)$ are response functions for the respective foils and $g(q,t_s + t)$ and $g(q,t_s)$ are response functions of the sample, where $t_s$ is the start time triggered when the electronic prompt signal reaches the APD detector. The flight time of radiation in free space is neglected. Details of these response functions will be further discussed in Section 2.3.2.

The total scattering probability amplitude is

$$W(t) = W_1(t) + W_2(t) + W_3(t) + W_4(t).$$ (2.54)
The scattering intensity is

\[ I(t) \propto W(t)W^*(t) = \left| W(t) \right|^2 \]

\[ = \left[ W_1(t) + W_2(t) + W_3(t) + W_4(t) \right] \left[ W_1^*(t) + W_2^*(t) + W_3^*(t) + W_4^*(t) \right] , \]

Where \( W^*(t) \) is the complex conjugate of \( W(t) \). The \( W_1(t) \) term represents the electronic prompt pulse which triggers the APD to start collecting data and is electronically block preventing the detector from becoming oversaturated, therefore we can ignore this term. For this experiment the spectral lines from the foils are widely separated and do not overlap, therefore the radiative coupling term, \( W_4(t) \) is small and can be ignored, see Figure 2.9.

Thus, working in the quantum beat (QB) regime, we only need to consider the terms \( W_2(t) \) and \( W_3(t) \).

Therefore, the scattering intensity is:

\[ I(t) = \text{Red terms} \]

\[ + \text{Blue terms} \]

\[ + \text{Green terms} \]

\[ + \text{Orange terms} \]
Figure 2.9: Mössbauer spectrum for $\alpha^{57}$Fe and stainless-steel foils. The spectral lines of $\alpha^{57}$Fe are widely separated from that of SS yielding very little overlap. Thus, the radiative coupling term, $W_4(t)$, can be ignored.

Using $W_2(t)W_3^*(t) + W_2^*(t)W_3(t) = 2 \text{Re} \left[ W_2(t)W_3^*(t) \right]$ gives

$$I(t) = W_2(t)W_3^*(t) + 2 \text{Re} \left[ W_2(t)W_3^*(t) \right] + W_3(t)W_3^*(t)$$

$$= \left\{ g(q, t_s + t)G_{Fe}(t)\left[e^{-i\omega_1 t} + e^{-i\omega_2 t}\right] \right\} \left\{ g^*(q, t_s + t)G_{Fe}(t)e^{i\omega_1 t} \right\}$$

$$+ 2 \text{Re} \left[ \left\{ g(q, t_s + t)G_{Fe}(t)\left[e^{-i\omega_1 t} + e^{-i\omega_2 t}\right] \right\} \left\{ g^*(q, t_s)G_{SS}(t)e^{i\omega_3 t} \right\} \right]$$

$$+ \left\{ g(q, t_s)G_{SS}(t)e^{-i\omega_3 t} \right\} \left\{ g^*(q, t_s)G_{SS}(t)e^{i\omega_3 t} \right\}$$
Simplifying gives

\[ I(t) = 2 \left[ g(q, t_s + t) G_{Fe}(t) \right]^2 \left\{ 1 + \cos \left[ (\omega_1 - \omega_2) t \right] \right\} \]

\[ + 2 \text{Re} \left\{ g(q, t_s + t) G_{Fe}(t) \left[ e^{-i\omega_1 t} + e^{-i\omega_2 t} \right] \right\} \left\{ g^*(q, t_s) G_{SS}^*(t) e^{i\omega_1 t} \right\} \]

\[ + \left| g(q, t_s) G_{SS}(t) \right|^2 \]

(2.55)

Expanding the middle term of Equation (2.55), \( 2 \text{Re} \left[ W_2(t) W_3^*(t) \right] \) yields

\[ W_2(t) W_3^*(t) = \left\{ g(q, t_s + t) G_{Fe}(t) \left[ e^{-i\omega_1 t} + e^{-i\omega_2 t} \right] \right\} \left\{ g^*(q, t_s) G_{SS}^*(t) e^{i\omega_1 t} \right\} \]

\[ = \left[ g(q, t_s + t) g^*(q, t_s) G_{Fe}(t) G_{SS}^*(t) \right] \left( e^{-i\omega_1 t} + e^{-i\omega_2 t} \right) e^{i\omega_1 t} \]

The product \( g(q, t_s + t) g^*(q, t_s) \) has Hermitian symmetry.[21] Since liquids in general have inversion and time reversal symmetry the product is a real function.

\[ W_2(t) W_3^*(t) = \ldots \left( e^{-i\omega_1 t} + e^{-i\omega_2 t} \right) e^{i\omega_1 t} \]

\[ = \ldots \left( \cos [-\omega_1 t] + i \sin [-\omega_1 t] + \cos [-\omega_2 t] + i \sin [-\omega_2 t] \right) \left( \cos [\omega_1 t] + i \sin [\omega_1 t] \right) \]

\[ = \ldots \left( \cos [\omega_1 t] - i \sin [\omega_1 t] + \cos [\omega_2 t] - i \sin [\omega_2 t] \right) \left( \cos [\omega_1 t] + i \sin [\omega_1 t] \right) \]

\[ = \ldots \left( \cos [\omega_1 t] \cos [\omega_3 t] - i \sin [\omega_1 t] \cos [\omega_3 t] + \cos [\omega_2 t] \cos [\omega_3 t] - i \sin [\omega_2 t] \cos [\omega_3 t] \right) \]

\[ + i \cos [\omega_1 t] \sin [\omega_1 t] + i \cos [\omega_3 t] \sin [\omega_1 t] + i \cos [\omega_2 t] \sin [\omega_3 t] + \sin [\omega_1 t] \sin [\omega_3 t] \]

Rearranging terms into real and imagery parts

\[ = \ldots \left[ \cos [\omega_1 t] \cos [\omega_3 t] + \sin [\omega_1 t] \sin [\omega_3 t] \right] \left[ \cos [\omega_2 t] \cos [\omega_3 t] - \sin [\omega_2 t] \sin [\omega_3 t] \right] \]

\[ - i \left[ \sin [\omega_1 t] \cos [\omega_3 t] - \cos [\omega_1 t] \sin [\omega_3 t] + \sin [\omega_2 t] \cos [\omega_3 t] - \cos [\omega_2 t] \sin [\omega_3 t] \right] \]
Now taking twice the real part, defining $\Omega = \omega_2 - \omega_1$ and for the special case where $\omega_3$ is midway between $\omega_1$ and $\omega_2$, $\frac{\Omega}{2} = \omega_2 - \omega_3 + \omega_{\text{IS}} = \omega_3 - \omega_1 + \omega_{\text{IS}}$, as shown in Figure 2.10 ($\omega_{\text{IS}}$ is the isomer shift and will account for any offset from $\omega_3$), gives:

$$2 \Re [W_2(t)W_3^*(t)] = 2[\ldots](\cos[(\omega_1 - \omega_3)t] + \cos[(\omega_2 - \omega_3)t])$$

$$= 2[\ldots]\left(\cos\left(\omega_2 - \Omega - \omega_2 - \omega_{\text{IS}} + \frac{\Omega}{2}t\right) + \cos\left(\frac{\Omega}{2} - \omega_{\text{IS}}\right)t\right)$$

$$= 2[\ldots]\left(\cos\left(-\frac{\Omega}{2} - \omega_{\text{IS}}\right)t\right) + \cos\left(\frac{\Omega}{2} - \omega_{\text{IS}}\right)t\right)$$

$$= 4[\ldots]\left(\cos\left(\frac{\Omega}{2}t\right)\cos[\omega_{\text{IS}}t]\right)$$

$$= 4g(q, t_s + t)g^*(q, t_s)G_{\text{Fe}}(t)G_{\text{SS}}(t)\cos\left[\frac{\Omega}{2}t\right]\cos[\omega_{\text{IS}}t]\right)$$

(2.56)

Substituting Equation (2.56) into Equation (2.55) gives the following equation for the intensity:

$$I(q, t) = \left|2g(q, t_s + t)G_{\text{Fe}}(t)\right|^2\left\{1 + \cos[(-\Omega)t]\right\} + \left|g(q, t_s)G_{\text{SS}}(t)\right|^2$$

$$+ 4g(q, t_s + t)g^*(q, t_s)G_{\text{Fe}}(t)G_{\text{SS}}(t)\cos\left[\frac{\Omega}{2}t\right]\cos[\omega_{\text{IS}}t]\right)$$

(2.57)

### 2.3.2 The response functions of the foils and sample

#### 2.3.2.1 Fe and SS Foils

The functions $G_{\text{Fe}}(t)$ and $G_{\text{SS}}(t)$ are the impulse response functions for $\alpha^{57}\text{Fe}$ and stainless-steel foils resulting from an incident synchrotron x-ray pulse approximated as a delta function in time [33, 34]:


Figure 2.10: An $\alpha$-$^{57}$Fe two-line spectrum separated by $\Omega = \omega_2 - \omega_1$ (red curves). The SS single line spectrum (blue curve) is separated from the red curves by $\Omega/2 = \omega_2 - \omega_3 + \omega_{IS} = \omega_3 - \omega_1 + \omega_{IS}$.

\[
G_{\text{Fe}}(t) = -\frac{T_{\text{Fe}}}{2\tau} e^{-\frac{t}{\tau}} \frac{J_1\left(\sqrt{t T_{\text{Fe}}} / \tau\right)}{\sqrt{t T_{\text{Fe}}} / \tau} [e^{-i\omega_1 t} + e^{-i\omega_2 t}], \quad (2.58a)
\]

\[
G_{\text{SS}}(t) = -\frac{T_{\text{SS}}}{2\tau} e^{-\frac{t}{\tau}} \frac{J_1\left(\sqrt{t T_{\text{SS}}} / \tau\right)}{\sqrt{t T_{\text{SS}}} / \tau} [e^{-i\omega_3 t}], \quad (2.58b)
\]

where the effective thickness is

\[
T = n \sigma_0 f_{LM} d. \quad (2.59)
\]
The effective thickness for iron foil is $T_{Fe}$ and for stainless-steel foil is $T_{SS}$, where $n$ is the number of nuclei per unit area, $\sigma_0$ is the Mössbauer absorption cross section, $f_{LM}$ is the Lamb-Mössbauer factor, and $d$ is the physical thickness of the foil. The radiative lifetime of the nuclear excited state is $\tau = \frac{\hbar}{\Gamma_0} = 141.1$ ns, where $\Gamma_0 = 4.67$ neV is the natural linewidth of an $^{57}$Fe nucleus. $J_1$ is a Bessel function of the first kind (this gives rise to dynamical beats, or “Bessel beats”, in the time spectra). The response function for a magnetized $\alpha$-$^{57}$Fe foil has two nuclear resonance frequencies $\omega_1$ and $\omega_2$, where $\Omega$ in Equation (2.68) is given by $\Omega = \omega_2 - \omega_1$. The two nuclear transition frequencies ($\Delta m = 0$) were achieved by magnetizing the iron foil with an external magnetic field perpendicular to both the incident x-ray direction ($\mathbf{H} \perp \mathbf{k}$) and polarization ($\mathbf{H} \perp \mathbf{σ}$). Stainless steel is paramagnetic and was modeled to have only one resonance frequency $\omega_3$. The value of $\omega_{IS}$ in Equation (2.68) is given by $\omega_{IS} = \omega_3 - \frac{\omega_2 + \omega_1}{2}$ and is a slight frequency off-set due to the isomer shift of stainless steel relative to $\alpha$-$^{57}$Fe.

### 2.3.2.2 Liquid sample dynamics

When a sample (such as a liquid) is placed between the two arms of the interferometer, a change in the quantum beat pattern is observed. This change contains information about the relaxation dynamics of the sample. The interference spectrum, when considering only the “Quantum Beat” regime, is modulated by the static structure factor $F(q, 0)$ and the dynamic intermediate scattering function $F(q, t)$. These functions are related to the quasi-elastic scattering response function of the liquid sample. The relationship can be found
by examining the time dependent scattering intensity, similar to the procedure outlined in Section 2.1.1:

\[
I(q, t) \approx \left| \frac{A}{R} e^{-ik'R} \sum_i f_i(q) e^{-iq'r_i(t)} \right|^2 \\
= \frac{A^2}{R^2} \left\langle \sum_{i,j} f_i(q)f_j(q) e^{-iq'r_i(t_s)}e^{iq'r_j(t_s+t)} \right\rangle,
\]

(2.60)

where \(\langle \ldots \rangle\) is a time or thermodynamic ensemble average. Normalizing over the static self scattering intensity, Equation (2.24), and assuming all the particles are identical results in the intermediate scattering function, \(S(q, t)\). Then defining \(F(q, t) \equiv S(q, t)\), to prevent confusion with the dynamic structure factor \(S(q, \omega)\) when \(\omega\) and \(t\) are both equal to zero, results in

\[
F(q, t) = \frac{1}{N} \left\langle \sum_{i,j} e^{-iqr_i(t_s) - r_j(t_s+t)} \right\rangle \\
= \frac{1}{N} \sum_{i,j} \int_V dr e^{-iq\cdot r} \left\langle \delta \left[ r - \{r_i(t_s) - r_j(t_s+t)\} \right] \right\rangle \\
F(q, t) = \int_V dr e^{-iq\cdot r} G(r, t)
\]

(2.61)

(2.62)

Thus, the dynamic intermediate scattering function, \(F(q, t)\), is the Fourier transfer of the pair distribution function, \(G(r, t)\).

The dynamic intermediate scattering function is proportional to the normalized time dependent scattering intensity by

\[
F(q, t) \equiv \frac{I(q, t)}{I_s(q, 0)}
\]

(2.63)
where substituting Equation (2.60) into the above equation is

$$F(q, t) = \frac{1}{\sum_i f_i(q)^2} \left< \sum_i f_i(q) f_j(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i(t_s)} e^{i\mathbf{q} \cdot \mathbf{r}_j(t_s + t)} \right>$$

$$= \left< \frac{\sum_i f_i(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i(t_s)}}{\sqrt{\sum_i f_i(q)^2}} \sum_j f_j(q) e^{i\mathbf{q} \cdot \mathbf{r}_j(t_s + t)} \right> \left( \frac{1}{\sqrt{\sum_i f_i(q)^2}} \right)$$

(2.64)

If all the particles are identical then Equation (2.64) reduces to Equation (2.61). Using Equation (2.49) to express the exponentials in terms of $g(q, t)$ for gives

$$F(q, t) = \frac{1}{\sum_i f_i(q)^2} \left< g(q, t_s) g^*(q, t_s + t) \right>$$

(2.65)

for a uniform liquid where all particles are identical. Then the response function for a uniform liquid can be written as $g(q, t_s) = \sum_i f_i(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i(t_s)}$ and $g(q, t_s + t) = \sum_i f_i(q) e^{-i\mathbf{q} \cdot \mathbf{r}_i(t_s + t)}$.

If $t = 0$, the dynamic intermediate scattering function, $F(q, t)$, becomes the static structure factor, $F(q, 0)$:

$$F(q, 0) = \frac{\left< g(q, t_s) g^*(q, t_s) \right>}{\sum_i f_i(q)^2} = \frac{\left< |g(q, t_s)|^2 \right>}{\sum_i f_i(q)^2} = \frac{\left< |g(q, t_s + t)|^2 \right>}{\sum_i f_i(q)^2}$$

(2.66)

The last equality is valid when averaging over particular times $t_s$ or $t_s + t$ are identical.

Figure 2.11 simulates snapshots of the location of the particles at times $t_s$ and $t_s + t$ inside a liquid sample. Figure 2.11(a) shows the position of all the particles when the prompt pulse triggers the APD detector to start collecting data. This defines the start time $t_s$. The electronic prompt scattering from the charge distribution in Figure 2.11(a) gives rise to the static structure factor $F(q, 0)$. Figure 2.11(b) shows the positions of the particles at some later time $t_s + t$ when nuclear resonance scattering occurs. Nuclear resonance scattering from
the charge distribution in Figure 2.11(b) gives rise to the dynamic intermediate scattering function $F(q, t)$. The intermediate scattering function is the sum of the time-dependent phase factors, $e^{i\phi_{ij}(t)}$, for each pair of particles,

$$F(q, t) = \frac{1}{N} \left\langle \sum_{i,j} e^{-i\mathbf{q} \cdot [\mathbf{r}_i(t_s) - \mathbf{r}_j(t_s + t) - \mathbf{r}_i(t_s) + \mathbf{r}_j(t_s) + t]} \right\rangle = \frac{1}{N} \sum_{i,j} e^{i\phi_{ij}(t)}$$  \hspace{1cm} (2.67)

Note that the terms $e^{i\phi_{ii}(t)} = 1$.

(a) Snapshot of the positions of the particles at time $t_s$ when the SR pulse triggers the detector.  \hspace{1cm} (b) Snapshot of the positions of the particles at some later time $t_s + t$.

Figure 2.11: (a) Static scattering and (b) time dependent scattering from a sample containing $N$ number of particles.
Finally, the interference spectrum, when considering only the “Quantum Beat” regime, using the dynamic intermediate scattering function and the static structure factor is

\[ I(q, t) = F(q, 0) \left[ 2 \left| G_{\text{Fe}}(t) \right|^2 \left( 1 + \cos[\Omega t] \right) + \left| G_{\text{SS}}(t) \right|^2 \right] \]

\[ + 4G_{\text{Fe}}(t)G_{\text{SS}}(t)F(q, t) \cos \left( \frac{\Omega t}{2} \right) \cos \left( \omega_{\text{IS}} t \right), \]

where all of the molecules are considered identical for a uniform sample.

\[ \text{(2.68)} \]

### 2.3.3 Final NR-TDI Intensity Equation

Factoring out \( F(q, 0) \) from Equation (2.68) and adding a term \( f_{\Delta E}(q) \) to describe electronic absorption through the \( ^{57}\text{Fe} \) foil gives:

\[ I(q, t) = F(q, 0) \left[ 2 \left| G_{\text{Fe}}(t) \right|^2 \left( 1 + \cos[\Omega t] \right) + f_{\Delta E} \left| G_{\text{SS}}(t) \right|^2 \right] \]

\[ + 4G_{\text{Fe}}(t)G_{\text{SS}}(t)F(q, t) \frac{F(q, t)}{F(q, 0)} \cos \left( \frac{\Omega t}{2} \right) \cos \left( \omega_{\text{IS}} t \right) \].

\[ \text{(2.69)} \]

The additional term \( f_{\Delta E}(q) \) is added as a fitting parameter depending on the sample properties and bandwidth of the synchrotron radiation interacting with just the SS foil.[25, 26] This term is a fraction of the dynamic structure factor overlapping with the spectrum of the SR pulse.[26]
In this thesis I model the normalized intermediate scattering function with the KWW stretched exponential, Equation (2.45). This model is used to describe the molecular dynamics of the liquid glycerol used in this thesis,

\[
\frac{F(q, t)}{F(q, 0)} = f_q e^{-\left(\frac{t}{\tau_K}\right)^\beta}
\]

with \(0 < \beta < 1\),

where \(\tau_K\) is the relaxation time, \(\beta\) is the stretching coefficient, \(F(q, 0)\) is the static structure factor, and \(f_q\) is non-ergodicity factor [25, 26]. The stretching coefficient is fixed with \(\beta = 0.6\) based on the trapping model in three-dimensional system[27] and other experimental results[25, 26]. The intermediate scattering function describes the randomness the time-dependent scattering phase factors shown in Figure 2.11(b). It’s inverse Fourier transform gives the pair distribution function which describes the molecular configuration of a sample.[35] The momentum transfer \(q\) is related to the spatial scale \(d\) of the electron density in the form \(q = \frac{2\pi}{d}\).[25] The relaxation time \(\tau_K\) is used to describe the dynamics of the liquid sample, and it is determined by observing the change in the coherence of the intensity spectrum.

The relaxation time, \(\tau_K\), is related to the diffusion constant, \(D\), by \(\tau_K = \frac{1}{Dq^2}\). The relaxation time is also related to the viscosity by the Stokes–Einstein equation \(D = \frac{k_B T}{6\pi \eta r}\), where \(k_B\) is Boltzmann’s constant, \(T\) is absolute temperature, \(\eta\) is the dynamic viscosity, and \(r\) is the radius of the spherical particle.[36, 37]

The final working equation used to measure the intensity as function of momentum transfer and time is

\[
I(q, t) = F(q, 0) \left[2 \left| G_{Fe}(t) \right|^2 \left(1 + \cos[\Omega t]\right) + f_{\Delta E}(q) \left| G_{ss}(t) \right|^2 \right] + 4 G_{Fe}(t) G_{ss}(t) f_q e^{-\left(\frac{t}{\tau_K}\right)^\beta} \cos \left[\frac{\Omega t}{2}\right] \cos [\omega_{ss} t].
\]  

(2.70)
2.4 Mössbauer Effect

The Mössbauer effect (or recoil-free nuclear gamma resonance emission and absorption) was discovered in 1957 during Rudolf Mössbauer’s graduate work. It involves the emission and absorption of gamma rays from an excited nucleus. When gamma rays are emitted from an excited nucleus, it must recoil due to the conservation of momentum. If the recoil energy is larger than the natural line width of the target’s nucleus there will be no absorption of the gamma photon. This problem is avoided by placing the emitting or absorbing nuclei inside a crystal lattice. This NR-TDI experiment takes full advantage of the coherence from the Mössbauer effect using it to measure the loss of coherence inside a liquid sample.

2.4.1 Typical Mössbauer Experimental Setup

A typical Mössbauer spectroscopy experiment uses a radioactive source, an absorber, and a photon detector, Figure 2.12. A photon is a type of elementary particle best described by quantum mechanics and exhibits both wave and particle properties. The photon is generated by the decay of a $^{57}$Co source when the nucleus goes from an excited state to a ground state. Doppler shifting the source by a Mössbauer transducer allows one to scan across the energy spectrum of the absorber.
2.4.1.1 Electron Capture

If a source has a nucleus that is deficient in neutrons or rich in protons, then a core electron can be captured resulting in a proton transitioning to a neutron. The most common Mössbauer isotope is $^{57}$Fe, which has the following electron capture reaction:

$$^{57}\text{Co}_{27} + e \rightarrow ^{57}\text{Fe}^*_{26},$$

(2.71)

where the $^{57}$Fe* is in a nuclear excited state. Three gamma rays are emitted (14.4129, 122.0614, and 136.4743 keV) when the system decays to a stable ground state, shown in Figure 2.13. The most commonly used gamma ray for the Mössbauer effect has an energy $E_\gamma = 14.4$ keV.

2.4.1.2 Natural Line Width

Radioactive decay is a statistical process where, if there are $N$ number of radioactive nuclei at some time $t$, then the number of decays $dN$ in a given interval time $dt$ will be proportional to $N$ by:

$$dN = -\lambda N \, dt,$$

(2.72)
Figure 2.13: The decay of $^{57}\text{Co}$ to stable $^{57}\text{Fe}$. The 14.4 keV ray is the most common Mössbauer photon.

where $\lambda$ is a constant of proportionality (called the decay rate).

The decay of a radioactive substance follows the exponential law

$$N = N_0 e^{-\lambda t} \quad (2.73)$$

where $N$ is the number of atoms in the initial state at time $t$, $N_0$ is the number of atoms at $t = 0$, and $\lambda$ is the decay rate characterized by the radioactive material. The half-life $t_{1/2}$ is found when the initial number of atoms, $N_0$, is reduced by half:

$$\frac{1}{2} N_0 = N_0 e^{-\lambda t_{1/2}}$$

$$\log \left[ \frac{1}{2} \right] = -\lambda t_{1/2}$$

$$t_{1/2} = \frac{0.693}{\lambda} \quad (2.74)$$
For $^{57}$Fe the nuclear transition having energy $E_\gamma = 14.4\,\text{keV}$ has a very narrow energy line width of approximately $5\,\text{neV}$. This natural line width, $\Gamma_0$, is determined by the mean life of the nuclear state and the Heisenberg uncertainty principle ($\Delta E \Delta t > \frac{\hbar}{2}$):

$$\Gamma_0 \tau = \hbar$$  

(2.75)

where $\Delta E$ is the half width at half-maximum, $\frac{\Gamma_0}{2}$ and $\Delta t$ is the radiative lifetime $\tau$. The value $\hbar = 6.582,119 \times 10^{-16}\,\text{eV}\,\text{s} = 658.2119\,\text{neV}\,\text{ns}$ is the reduced Planck’s constant. Consider the first excited of $^{57}$Fe which has a $t_{1/2} = 97.7\,\text{ns}$ or $\tau = 141.1\,\text{ns}$, then $\Gamma_0 = 4.67\,\text{neV}$ or $0.0965\,\text{mm}\,\text{s}^{-1}$. This line width of $\Gamma_0 = 4.67\,\text{neV}$ is infinitesimally small compared to the gamma ray energy of $E_\gamma = 14.4\,\text{keV}$ (by $\approx 10^{13}$ orders of magnitude).

Table 2.1: Comparison between a modern SR source and a commercially available $^{57}$Co source with 100 mCi activity. The SR data includes losses in x-ray optics.[38]

<table>
<thead>
<tr>
<th>Property</th>
<th>SR</th>
<th>$^{57}$Co source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral flux $(s^{-1},\text{eV}^{-1})$</td>
<td>$3 \times 10^{12}$</td>
<td>$2.5 \times 10^{10}$</td>
</tr>
<tr>
<td>Brightness $(s^{-1},\text{eV}^{-1},\text{sr}^{-1})$</td>
<td>$1 \times 10^{22}$</td>
<td>$2.5 \times 10^{13}$</td>
</tr>
<tr>
<td>Spectral flux density $(s^{-1},\text{eV}^{-1},\text{mm}^{-2})$</td>
<td>$5 \times 10^{12}$</td>
<td>$2 \times 10^{5}$</td>
</tr>
<tr>
<td>Beam size focused</td>
<td>$20 \times 15,\mu\text{m}$</td>
<td>–</td>
</tr>
<tr>
<td>Beam size unfocused</td>
<td>$1.2 \times 0.4,\text{mm}$</td>
<td>$25 \times 25,\text{mm}$</td>
</tr>
</tbody>
</table>

Comparing SMS with traditional methods of Mössbauer spectroscopy is shown in Table 2.1. The $\gamma$ rays emitted by a radioactive source are very different than the $\gamma$ rays emitted by a synchrotron source. However, both sources can be used for Mössbauer experiments for measuring the hyperfine parameters. The synchrotron emits a series of periodic short, collimated pulses of x-rays. Whereas a radioactive source emits photons at random times and in all directions. A traditional Mössbauer experiment is a measurement in frequency space (or energy), whereas an SMS experiment is a measurement in time. Figure 2.14 shows simulations for both traditional and SMS experiments for a magnetized $\alpha-^{57}$Fe foil.
Figure 2.14: The top image is a traditional Mössbauer spectroscopy measurement and the bottom is a Synchrotron Mössbauer Spectroscopy measurement with the plots on the right showing a typical spectrum for a magnetized $\alpha-^{57}\text{Fe}$ foil.

The advantage of using synchrotron Mössbauer spectroscopy (SMS) over traditional Mössbauer spectroscopy is that the intensity of the beam is seven orders of magnitude brighter than a radioactive source and is highly collimated. The x-ray beam can be focused using Kirkpatrick–Baez mirrors to about a 15 $\mu$m by 20 $\mu$m spot size. The major advantage of using traditional Mössbauer spectroscopy is the accessibility to the experimental setup and equipment (as long as radiative sources are available). A major disadvantage of using traditional Mössbauer spectroscopy is that the collection times for a spectrum are much longer because most of the data is background. For SMS measurements the background is minimal.
2.4.2 Source arm: $\alpha^{-57}$Fe foil

A typical Mössbauer experiment has a $^{57}$Co source attached to a Mössbauer drive that translates the source over a range of velocities around $\pm 10 \text{ mm s}^{-1}$. If the absorber contains $^{57}$Fe, then the detector will count the number of gamma rays transmitted through the foil at each velocity. The spectrum for this absorber is shown in Figure 2.15, where the six peaks represent the magnetic hyperfine splitting for a 2 $\mu$m cold roll enriched $\alpha^{-57}$Fe foil with texture used in my thesis.

![Mössbauer spectrum](image)

Figure 2.15: The Mössbauer spectrum for $\alpha^{-57}$Fe foil.

All electrons, protons, and neutrons have an inherent angular momentum about their own axis, which gives the nuclei their own angular momentum with spin $I$. From quantum mechanics the allowable nuclear spin states are quantized and split into $2I + 1$ sub-energy
levels. These sub-energy levels can only have values of \( m_I = I, I - 1, \ldots, -I \). The ground state for \( ^{57}\text{Fe} \) has spin \( I_g = \frac{1}{2} \), giving it two substates with \( m_I = +\frac{1}{2} \) and \( m_I = -\frac{1}{2} \). For the excited state \( ^{57}\text{Fe} \) has spin \( I_e = \frac{3}{2} \), giving it four substates with \( m_I = +\frac{3}{2} \), \( m_I = +\frac{1}{2} \), \( m_I = -\frac{1}{2} \), and \( m_I = -\frac{3}{2} \). The selection rules state that the only possible transitions for a photon that carries spin 1 are \( \Delta m = +1, 0, -1 \).[16] Therefore, the possible transitions lines for magnetic hyperfine splitting are shown in Figure 2.16, these lines correspond to the numbered transmission peaks in Figure 2.15.

\[
\begin{align*}
E_{g,+\frac{1}{2}} &= +92.2 \text{ neV} \\
E_{g,-\frac{1}{2}} &= -92.2 \text{ neV} \\
E_{e,+\frac{3}{2}} &= +157.6 \text{ neV} \\
E_{e,+\frac{1}{2}} &= +52.5 \text{ neV} \\
E_{e,-\frac{1}{2}} &= -52.5 \text{ neV} \\
E_{e,-\frac{3}{2}} &= -157.6 \text{ neV}
\end{align*}
\]

\( \Delta m = -1, 0, +1 \)

\( m_I \)

Figure 2.16: Energy level diagram for the magnetic and quadrupole splitting for \( \alpha^{-57}\text{Fe} \) foil.

The first (source) arm of the NR-TDI setup is a magnetized \( \alpha^{-57}\text{Fe} \) foil, Figure 2.17. A two-line nuclear resonance spectrum can be achieved by magnetizing the \( \alpha^{-57}\text{Fe} \) foil with
an external magnetic field perpendicular to both the incident x-ray direction ($\mathbf{H} \perp \mathbf{k}$) and polarization ($\mathbf{H} \perp \mathbf{\sigma}$). By magnetizing the $^{57}$Fe in those directions chooses only the $\Delta m = 0$ cases, lines 2 and 5 in Figures 2.15 and 2.16. CONUSS (program written by Wolfgang Sturhahn for nuclear resonant scattering of synchrotron radiation[39]) was used to simulate the energy spectrum for the magnetized $^{57}$Fe foil, shown in Figure 2.18. The separation between the peaks 2 and 5 is defined by $\Omega = \omega_2 - \omega_1$ which determines the beat frequency in the time domain.

The value of $\Omega$ is calculated from the Hamiltonian for the magnetic dipole

$$\mathcal{H} = -\frac{\mu_N g_L m_i H}{I}$$

(2.76)

where $g_L$ is the nuclear Landé g-factor, $\mu_N \equiv \frac{e\hbar}{2m_p} = 31.5245 \text{ neV T}^{-1}$ is the nuclear Bohr magneton, and $H$ is the internal magnetic field the nucleus experiences (for $^{57}$Fe $H = 33 \text{ T}$).[40] If an external magnetic field is applied to the foil the new magnetic field becomes the effective magnetic field ($H_{\text{eff}}$) which is the difference between $H$ and the external magnetic field strength. The nuclear magnetic moment of $^{57}$Fe aligns itself opposite to the applied magnetic field. The external magnetic field used in this experiment to create a two-line spectrum was $0.736 \text{ T}$ rare earth magnet giving an effective magnetic field of $H_{\text{eff}} = 32.264 \text{ T}$. 
Figure 2.18: Simulated energy spectrum for magnetized $\alpha^{57}$Fe foil using CONUSS.

The Landé g-factor of $^{57}$Fe foil for ground state is $g_\text{g} = 0.09069$ and for the excited state is $g_\text{e} = -0.1549$. The energy of the ground state is

$$E_{g,m_I=\pm \frac{1}{2}} = -\frac{\mu_N g_\text{g} m_I H_{\text{eff}}}{I_\text{g}} = \mp 92.2 \text{ neV}$$  \hspace{1cm} (2.77)

and the energy from the splitting due to the internal magnetic field of the excited state is

$$E_{e,m_I=\pm \frac{1}{2}} = -\frac{\mu_N g_\text{e} m_I H_{\text{eff}}}{I_\text{e}} = \pm 52.5 \text{ neV}$$  \hspace{1cm} (2.78)

$$E_{e,m_I=\pm \frac{3}{2}} = -\frac{\mu_N g_\text{e} m_I H_{\text{eff}}}{I_\text{e}} = \pm 157.6 \text{ neV}$$  \hspace{1cm} (2.79)
Energy for transition lines 2 and 5 when $\Delta m = 0$ in Figure 2.18 is

$$E_{\odot} = E_g + E_{g,-\frac{1}{2}} - \left( E_e + E_{e,-\frac{1}{2}} \right) = E_g - E_e + E_{g,-\frac{1}{2}} - E_{e,-\frac{1}{2}}$$

$$E_{\odot} = E_g + E_{g,+\frac{1}{2}} - \left( E_e + E_{e,+\frac{1}{2}} \right) = E_g - E_e + E_{g,+\frac{1}{2}} - E_{e,+\frac{1}{2}}$$

The energy difference between transition lines 2 and 5 is

$$\Delta E_{\odot \rightarrow \odot} = E_{g,,-\frac{1}{2}} - E_{e,-\frac{1}{2}} - E_{g,+\frac{1}{2}} + E_{e,+\frac{1}{2}}$$

$$\Delta E_{\odot \rightarrow \odot} = 289.5 \text{ neV}$$

(2.80)

The energy of a photon using the Planck–Einstein relation is

$$E = h\nu = \hbar\omega.$$  

(2.81)

This allows for the calculation of the beat frequency ($\Omega$) from the two-line spectrum between the ground and excited states.

$$\Omega = \frac{\Delta E_{\odot \rightarrow \odot}}{\hbar} = \frac{289.5 \text{ neV}}{658.212 \text{ neV ns}}$$

$$= 0.439 \ 852 \ \text{rad ns}^{-1} \ \text{or} \ 70.0046 \ \text{MHz} \ \text{or} \ 62.1\Gamma_0$$

The beat frequency determines the period in Figure 2.19 by the following equation.

$$T = \frac{1}{70.0046 \ \text{MHz}} = 14.2848 \ \text{ns}$$

(2.82)
Figure 2.19: (a) SMS measurement in the forward direction for magnetized $\alpha^{-57}\text{Fe}$ with $\mathbf{H} \perp \sigma$. (b) The green curve represents the residuals of the fit.

Figure 2.19(a) shows the SMS data of a magnetized $\alpha^{-57}\text{Fe}$ foil. The measured intensity for such a case in the forward direction ($q = 0$) is the first term from Equation (2.68) without the $F(q,0)$ term because that term comes from the sample

$$I(0,t) = 2 \left| G_{\text{Fe}}(t) \right|^2 \left(1 + \cos[\Omega t]\right).$$  \hspace{1cm} (2.83)

The red line in Figure 2.19(a) is the fit with an effective thickness for the Fe foil of $T_{\text{Fe}} = 15.2 \pm 0.1$ (corresponding to a foil thickness of $2.10 \pm 0.02 \mu m$) using Equation (2.59) and beat frequency of $\Omega = 69.8 \pm 0.1 \text{MHz}$ ($61.9 \pm 0.1 \Gamma_0$). The green line in Figure 2.19(b)
describes the standardized residuals for the fit, which is difference between the fit and data divided by the standard error for each residual. Using 33 T as the standard field for an α-Fe foil, the value of $\Omega$ indicates the applied external magnetic field was 0.82 T (close to the Hall probe measurement of 0.736 T for the external magnetic used in this experiment, see Figure 3.11(a)).

### 2.4.3 Analyzer arm: SS foil

Figure 2.20 shows the second (analyzer) arm of the NR-TDI setup is a single-line SS absorber. A simulation using CONUSS of the energy spectrum for the SS foil is shown in Figure 2.21. For stainless steel the isomer shift is $\omega_{\text{IS}} = -0.1 \text{ mm s}^{-1}$.

![Analyzer Arm](image)

Figure 2.20: SMS setup for SS foil in the forward direction.

The isomer shift results from a Coulombic interaction between the nuclear and electronic charge distributions of both the source and absorber. It is a function of the s-electronic charge density at the nucleus.[41] The shift in general will be the difference between the source’s and absorber’s isomer shifts.[42] Figure 2.22 is an energy diagram showing the isomer shifts of the source and absorber. The isomer shift can be either positive ($^{a}E_{\gamma} > ^{s}E_{\gamma}$) or negative ($^{a}E_{\gamma} < ^{s}E_{\gamma}$).[43]
The measured intensity for such a case in the forward direction \((q = 0)\) is the second term from Equation (2.68) without the \(F(q, 0)\) term because that term comes from the sample

\[
I(0, t) = \left| G_{ss}(t) \right|^2. \tag{2.84}
\]

Figure 2.23(a) shows the SMS data for the SS foil. Figure 2.21 is the energy domain representation of Fig. 2.23(a). The red line in Figure 2.23(a) is the fit with an effective thickness for SS foil of \(T_{ss} = 11.9 \pm 0.1\) (corresponding to a foil thickness of 0.9 \(\mu\)m using Equation (2.59)).
Figure 2.22: Energy level diagrams showing the isomer shift of the source and absorber.
Figure 2.23: (a) SMS measurement in the forward direction for SS. (b) The green curve represents the residuals of the fit.
2.4.4 Interferometer: $\alpha$-$^{57}$Fe and SS foils

The NR-TDI interferometer is shown in Figure 2.24, using a two-line magnetizing $\alpha$-$^{57}$Fe foil and a single-line stainless-steel (SS) foil. CONUSS used to simulate the energy spectrum for the $\alpha$-$^{57}$Fe and SS foils is shown in Figure 2.25.

The measured intensity in the forward direction for $^{57}$Fe and SS foils is

$$I(0, t) = 2\left|G_{Fe}(t)\right|^2 \left(1 + \cos[\Omega t]\right) + f_\alpha \left|G_{SS}(t)\right|^2 + 4f_\beta G_{Fe}(t)G_{SS}(t) \cos\left[\frac{\Omega}{2}t\right] \cos[\omega_{is} t]$$ (2.85)

Figure 2.26(a) shows the SMS data and the fit (red curve) for the $\alpha$-$^{57}$Fe and SS foils. Figure 2.25 is the energy domain representation of Figure 2.26(a). The fit resulted in a SS foil isomer shift of $\omega_{is} = -1.1 \pm 0.2$ MHz or $-0.09 \pm 0.01$ mm s$^{-1}$, $f_\alpha = 0.63 \pm 0.04$ and $f_\beta = 0.75 \pm 0.02$. The factors $f_\alpha$ and $f_\beta$ describe the loss of coherence due to the relative broadening of the linewidth of one absorber with respect to the other and electronic absorption.

The calibration of the foils and the fitting parameters are summarized in Table 2.2. The calibrations were completed in the forward direction where the momentum transfer is $q = 0$ nm$^{-1}$ and at room temperature. For all future fits where a liquid sample is inserted into the interferometer, the four parameters in Table 2.2 were always fixed.
Figure 2.25: Simulated energy spectrum for 2\(\mu\)m \(^{57}\)Fe and 0.9\(\mu\)m SS foils using CONUSS.

Table 2.2: Calculated fitting parameters for the \(\alpha\)-\(^{57}\)Fe and SS foils in the forward direction at room temperature.

<table>
<thead>
<tr>
<th>Fitting Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{Fe})</td>
<td>15.2 ± 0.1 (d_{Fe} = 2.10 \pm 0.02 \mu)m</td>
</tr>
<tr>
<td>(T_{SS})</td>
<td>11.8 ± 0.1 (d_{SS} = 0.87 \pm 0.01 \mu)m</td>
</tr>
<tr>
<td>(\Omega)</td>
<td>69.8 ± 0.1 MHz or 6.02 ± 0.08 mm s(^{-1})</td>
</tr>
<tr>
<td>(\omega_{IS})</td>
<td>−1.1 ± 0.2 MHz or −0.09 ± 0.01 mm s(^{-1})</td>
</tr>
</tbody>
</table>
Figure 2.26: (a) SMS measurement in the forward direction for \( \alpha-^{57}\text{Fe} \) and SS foils. (b) The green curve represents the residuals of the fit.
CHAPTER 3
NR-TDI EXPERIMENTAL SETUP

3.1 Advanced Photon Source

The Advanced Photon Source (APS) at Argonne National Laboratory provides ultrabright high-energy x-rays to be used for research in many different scientific disciplines. The process of creating these x-rays begins with a source of electrons emitted from a cathode through thermal emission by a filament when heated to 1000 °C. The electrons are accelerated by a linear accelerator (LINAC) to 450 MeV. From the LINAC the beam is injected into the particle accumulator ring (PAR) which compresses the long electron bunch of about 10 to 15 ns down to less than 1 ns. It also cleans the electron bunch removing any stray electrons before being delivered to the booster synchrotron. The booster ring accelerates the electrons from 450 MeV to 7 GeV, which are now traveling at > 99.999,999% the speed of light. The accelerating force is supplied by the electrical fields in four radio frequency cavities. The orbital path of the electrons is maintained by the bending and focusing magnets which increase the electron field strength when synchronized with the radio frequency fields. The 7 GeV electrons are injected into the storage ring, which has a circumference of 1104 m. An electromagnetic field focuses the electrons into a narrow beam which travels around the storage ring through vacuum chambers running through the centers of electromagnets. There are 40 straight sections at the APS, 5 sectors are used for beam injection and radio frequency equipment. The other 35 sectors are the individual beamlines used to the study all different types of sciences.
3.1.1 APS Timing Modes

This experiment was performed at Argonne National Laboratory at the APS using beamline 3-ID. This experiment used two of the five different timing modes. The majority of the measurements used the standard top-up (24 bunch) operating mode. This mode had a storage ring top-up fill pattern of 102 mA in 24 singlets having a bunch length of 33.5 ps and a bunch spacing of 153 ns, Figure (3.2). The other special operating mode used was hybrid fill, Figure (3.3). In this mode the storage ring top-up fill pattern was 102 mA with a single bunch containing 16 mA, which was isolated from the other bunches by a 1594 ns gap. The
remaining current was distributed into 8 groups (separated by 51 ns between each group) with 7 bunches in each group (separated by 2.84 ns between each bunch). The length for each group was 17 ns and the total length of the bunch train was 500 ns. Using the hybrid mode extends the time scale to approximately 1.6 µs, but reduces the number of photons by about one-third.

Figure 3.4 shows the electronics used for data collection. Starting with the bunch clock generators (BCG) which reads the zeroth pulse $P_0$ coming from the control room at the APS. This zeroth pulse completes one full revolution around the beam every 3.68 µs. The middle
bunch clock generator, B0, is inputted to a constant fraction discriminator (CFD) that converts the signal to a negative going nuclear instrumentation module (NIM) pulse before going to the logic unit (LU) input B. This logic unit creates an adjustable veto window used to remove the prompt pulses. The prompt pulse contains approximately $6.5 \times 10^9$ photon s$^{-1}$. Instead of starting the time-to-amplitude (TAC) with the prompt pulse, we use the delayed photons to start the TAC, Figure 3.5. The avalanche photodiode detector (APD) detects both the prompt and delay photons and amplifies the signal before converting it to a NIM pulse by the CFD which goes into input A of the LU starting the TAC. A second BCG (B1) delays the prompt pulse before going into the CFD and then to the output of the TAC, thereby stopping the measurement. The output of the TAC goes into the input of the analog-digital converter (ADC). The ADC converts the signal from the TAC into a digital signal read by the multichannel analyzer (MCA) which places the signal into one of 4096 channels, as shown in the MCA plot in the lower right-hand corner of Figure 3.4.
Figure 3.3: Special hybrid mode ring configuration used at the APS.
Figure 3.4: The electronics for NR-TDI at sector 3. The red line is the signal from the APD which starts the TAC. The solid black line is the signal from the bunch clock generator, B0, which blocks the prompt pulse (one of the 24 singlets). The dashed line is the signal from the other bunch clock generator, B1, that stops the TAC measurement. The ADC converts the analog voltage signal into a digital signal read by the MCA assigning a voltage to a channel and adding a count every time a voltage is measured to that channel. The plot in the lower right-hand corner is the data collected from the MCA.
Figure 3.5: The timing window for 24 bunch mode with prompts everything 153 ns (red peaks). The APD detects the delayed nuclear radiation (blue peak) starting the TAC measurement and stopping at the next prompt peak.
3.2 Converting MCA Data

The NR-TDI studies the diffusional molecular motion of a liquid sample by analyzing how the phases of the scattered x-rays interacted with each other inside the sample. The $\alpha^{57}$Fe foil produces a coherent reference spectrum that can interfere with the molecular motion of the sample destroying its coherence and SS foil acts as an analyzer. The destructive motion of the liquid sample can give inside about properties of it, such as its relaxation time. This process starts by evaluating the data collected from the MCA at the beamline for the $^{57}$Fe and SS foils in the forward direction ($q = 0 \text{ nm}^{-1}$). The raw data needs to be converted from channels to time outlined by the following method.

![Multichannel Analyzer (MCA) Data](image)

Figure 3.6: MCA data for the magnetized $\alpha$-$^{57}$Fe foil in the forward direction using 24 bunch mode.
All the data and fits followed the same fitting procedures outlined by the following. Figure 3.6 is the data for the magnetized \( \alpha^{57}\text{Fe} \) foil in the forward direction collected by the MCA. It needs to be converted from channels to time and the conversion factor used was 0.0489 ns/channel for standard operating mode (24 bunch mode). Recall from Section 3.1.1 where the APD collects delay nuclear radiation including the prompt peak which defines \( t_0 \). The electronics used veto windows to block the prompt count during data collection and remove those veto windows for a brief time to add it the data set. The APD normally records the delay nuclear radiation and the MCA assigns each one a channel based on its voltage. A simple program was written to find the prompt peak or assign the prompt peak as a specific channel. Assigning the prompt peak happens either when the prompt could not be found or if the prompt was not added to the MCA data set. Figure 3.6 shows the maximum counts occurring in channel 2750 for the \( \alpha^{57}\text{Fe} \) foil, which now determines the start time \( t_0 \). Each channel was subtracted from the prompt channel and multiple by 0.0489 ns/channel creating a raw data set of counts as a function of time in nanoseconds, the blue curve in Figure 3.7.

The data can be binned to reduce the minor scrutinization and uncertainties at the lower counting regions (usually at longer times for TDI). One way to bin the data, starts by choosing the number of channels to bin together. For 24 bunch mode a good bin size is 10. Which means taking a set of 10 sequential data points (times and counts), averaging the times together giving one time and summing the counts of those same 10 bins giving a new total count. This creates a new binned data point. This was done for every 10 channels of the entire data set of 4096 channels or times, creating a new binned data set (the green curve in Figure 3.7).

The green curve, in Figure 3.8(b), is the hybrid data for a bin size of 4 and using the conversion factor is 0.237 ns/channel. The benefit of the hybrid mode is the timing window is much longer with data being able to be collected up to 800 ns. The downfall is the number of prompts is reduced by approximately third, which decreases the delay counts. In the
forward direction during hybrid mode the delay counts were approximately 107 Hz (or 107 counts every second) for the 2 µm magnetized $\alpha$-\textsuperscript{57}Fe foil. Compared to same foil during 24 bunch mode with an approximate delay count of 1090 Hz (or 1090 counts every second). These counts are even lower after scattered from the sample.

### 3.2.1 Calibration foils

The calibration of the interferometer is accomplished in three separate measurements: (1) the magnetized $\alpha$-\textsuperscript{57}Fe foil in the forward direction, (2) the SS foil in the forward direction, and (3) both magnetized $\alpha$-\textsuperscript{57}Fe and SS foils in the forward direction. The first measurement gives the effective thickness $T_{Fe}$ and beat frequency $\Omega$ of the $\alpha$-\textsuperscript{57}Fe foil in Equation (2.83).
(a) MCA data for the magnetized $\alpha$-$^{57}$Fe foil in the forward direction using hybrid mode.

(b) SMS timing data for the magnetized $\alpha$-$^{57}$Fe foil in the forward direction using hybrid mode. The blue curve is raw data and the green curve is binned data having a bin size of 4.

Figure 3.8: Magnetized $\alpha$-$^{57}$Fe foil in the forward direction during hybrid operation mode.

The second measurement gives the effective thickness $T_{SS}$ of the SS foil in Equation (2.84). The third measurement gives the isomer shift $\omega_{IS}$ of the SS foil in Equation (2.85). All of these parameters were fitted using a Levenberg-Marquardt least squares fit routine where the uncertainties in the fit parameter were given by the covariance matrix.

Figure 3.9 shows the SMS data (blue points) for the three measurements and their corresponding simulated energy spectra. The red curves are the fits where the fitting parameters used are calibration parameters given in Table 2.2. The green curve describes the standardized residuals for the fit, which is the difference between the fit and data divided by the standard error for each residual.
Figure 3.9: All measurements were done in the forward direction. (a) Magnetized $\alpha$-$^{57}$Fe with $\mathbf{H} \perp \boldsymbol{\sigma}$, (a’') the two-line energy spectrum for magnetized $\alpha$-$^{57}$Fe (b) stainless-steel foil, (b’’) the single line energy spectrum for stainless steel, (c) the magnetized $\alpha$-$^{57}$Fe and stainless-steel foils, (c’’) the three-line energy spectrum for the $\alpha$-$^{57}$Fe and stainless-steel foils. The green curves are the respective residuals of the fit method.
### 3.3 Experimental setup at APS 3ID-B beamline

The NR-TDI setup used at sector 3 at the APS is shown in Figure 3.10. The x-ray beam was monochromated by a cryo-cooled Si(111) high-heat-load monochromator (HHL) and then by a Si multi-reflection high-resolution monochromator (HRM) reducing the energy band-pass to about $\Delta E = 1\text{ meV}$ at 14.4 keV. The x-ray beam goes through a 2 $\mu$m magnetized enriched $\alpha$-$^{57}$Fe foil, shown in Figure 3.11(a), with a magnetic field strength of 0.736 T at the center. The magnetic field was perpendicular to both the incident x-ray direction ($\mathbf{H} \perp \mathbf{k}$) and polarization ($\mathbf{H} \perp \mathbf{\sigma}$). The magnetic system was made from eight NdFeB permanent magnets (grade N42), as shown in Figure 3.11(b). A set of Kirkpatrick-Baez mirrors (KB) were used to focus the beam down to $15 \mu m \times 20 \mu m$ onto the sample. The photon flux on the sample was $3 \times 10^9$ photon/sec/meV. The sample was placed inside a temperature-controlled helium flow cryostat. The beam then goes through a 0.9 $\mu$m enriched $^{57}$Fe stainless-steel (SS) foil which acts like an analyzer. The 0.85 $\mu$m thick gold annular slit makes it possible to make high count rate measurements at specific $q$-values by adjusting the distance between the sample and the annular slit. The signal was collected using a Si APD detector with an active area of $1 \text{ cm} \times 1 \text{ cm}$ and a thickness of 200 $\mu$m. The detector has sub-ns time resolution and an efficiency of 40% at 14.4 keV.

![Diagram of NR-TDI setup for SMS with a magnetized $\alpha$-$^{57}$Fe foil, liquid sample, and a SS foil.](image)

Figure 3.10: NR-TDI setup for SMS with a magnetized $\alpha$-$^{57}$Fe foil, liquid sample, and a SS foil.
Figure 3.11: External 0.736 T magnetic used to magnetize the $\alpha^{57}$Fe foil used for NR-TDI.

3.3.1 Early attempts at NR-TDI

Recall Figure 2.1, where a typical x-ray scattering experiment consists of an incoming wave, $k$, and elastically scattered wave, $k'$, through an angle $2\theta$, with a momentum transfer

$$q = |k' - k| = \frac{4\pi}{\lambda} \sin \theta.$$  

The scattering intensity was measured as a function of $q$, $I(q)$. Figure 3.12 shows $S(q)$ for pure glycerol with the maximum scattering intensity occurring around $q = 14.25 \text{nm}^{-1}$ or $2\theta = 11.2^\circ$.

An early approach tried at the APS for NR-TDI measurements used a single APD detector as shown in Figure 3.13. The distance between the sample and APD detector is $L$ and $x$ is the transverse distance of the APD detector. The momentum transfer, $q$, is defined by...
Figure 3.12: The $S(q)$ intensity for pure glycerol (red curve) at room temperature. The data points indicate where NR-TDI momentum transfer measurements were taken ($q = 2, 5, 7, 10, 14, \text{and} 20 \text{ nm}^{-1}$). The blue circles are for the 1.0 mm annular slit and the error bars are the $q$-resolution for that particular momentum transfer.

the following equation using this geometry:

$$ q(x, L) = \frac{4\pi}{\lambda} \sin\left[\frac{1}{2} \tan^{-1}\left(\frac{x}{L}\right)\right], \quad (3.1) $$

where $\lambda = 0.086 \text{ nm}$ is the wavelength of the x-ray beam. To measure $q = 14.0 \text{ nm}^{-1}$ for a fixed $L = 75 \text{ cm}$, the transverse distance needs to be set around $x = 14.6 \text{ cm}$. Using this geometry, scattered x-rays will be collected in an annulus ring having an area of 91.7 cm$^2$ (assuming 1 cm slit aperture). The active diode area of the APD is 1 cm$^2$. With this geometry approximately 1% of the total x-rays scattered are being capture by the APD. This is the shaded region on the APD in Figure 3.13. This small area leads to low counting rates, but
Figure 3.13: The APD has a diode area of 1 cm$^2$ (shaded region). For $q = 14.0 \text{ nm}^{-1}$ and $L = 75 \text{ cm}$, we set $x = 14.6 \text{ cm}$. The area of the annulus is 91.7 cm$^2$.

with high $q$ resolution (Section 3.4.1 goes into more detail). Some previous experiments have used multiple detectors at multiple angles to combat the inherent low counting rates [8, 10]. We did preliminary measurements using three detectors at the same angle to increase the counting rate by a factor of 5 (we did not achieve this because of technical difficulties and only achieved a factor of 2-3). From these measurements we determined at least 10 APD detectors would be needed to achieve a counting rate high enough to do acceptable experiments. However, adding more detectors would greatly increase the complexity and expense of the experiment. As a result, we decided to employ an annular slit instead.
3.4 Gold annular slits

In an attempt to collect all the x-rays scattered at a particular $q$, a gold annular slit was fabricated. The annular slit could be positioned in front of an APD detector as shown in Figure 3.14. This allowed for the collection of 92% of the scattered x-rays instead of the 1% from the single detector setup shown in Figure 3.13. The gold tabs that held the central disk in place caused a loss of 8% of the scattered x-rays. This resulted in an increase in count rate of almost two orders of magnitude.

![Figure 3.14: Scattering setup for the gold annulus, where $L$ is the distance from the sample to the annulus and $x$ is the radius to the center of the slit. For the 1.0 mm wide annular slit the radius was $x = 4.0$ mm. To measure $q = 14.0 \pm 2.7$ nm$^{-1}$, $L$ must be fixed to 20.6 mm.](image)

A total of three annular slits were made for this experiment. Two of the annular slits with 1.0 mm and 0.5 mm apertures were made using wire electrical discharge machining (EDM). This technique uses a wire electrode to precisely cut contours into a workpiece. A third annular slit with 0.2 mm aperture was made using a rotating cutting tool. The annular slits were made from a gold foil approximately 20 mm $\times$ 20 mm and thickness of 85 $\mu$m. An extra
piece of gold was added to the center of the annular slit as a beamstop. The dimensions of the annular slits are shown in Figure 3.15. A custom mount was designed that attached to the APD allowing the annular slits to precisely be centered and placed close to the detector.

The choice of a 9 mm outside diameter ensured the entire area of the 10 mm × 10 mm APD diode was covered. The width of the slit was chosen based on calculations of the $\Delta q$ resolution.

![Figure 3.15: (a) 1.0 mm, (b) 0.5 mm, and (c) 0.2 mm aperture annular gold slits with a thickness of 85 µm and 20 mm × 20 mm area.](image)

### 3.4.1 Momentum resolution

The momentum resolution at the detector depends on several factors: (1) the distance from the sample $L$, (2) the thickness of the sample $d$, and (3) the width of the slit $s$. This is shown schematically in Figure 3.16, where $\theta$, $\theta_1$, and $\theta_2$ are given by:

$$ \theta = \frac{1}{2} \tan^{-1} \left[ \frac{x}{L} \right] $$  \hspace{1cm} $q$ centered angle \hspace{1cm} (3.2a)

$$ \theta_1 = \frac{1}{2} \tan^{-1} \left[ \frac{x - s/2}{L + d/2} \right] $$  \hspace{1cm} $q$ inside slit angle \hspace{1cm} (3.2b)

$$ \theta_2 = \frac{1}{2} \tan^{-1} \left[ \frac{x + s/2}{L - d/2} \right] $$  \hspace{1cm} $q$ outside slit angle \hspace{1cm} (3.2c)
and where $x$ is the distance from the center of the annulus to the center of the slit. The momentum resolution is:

$$\pm \Delta q = \frac{1}{2} \left\{ \frac{4\pi}{\lambda} \left( \sin \left[ \theta_2 + \frac{\alpha}{4} \right] - \sin \left[ \theta_1 - \frac{\alpha}{4} \right] \right) \right\}, \quad (3.3)$$

where $\alpha = 30 \, \mu \text{rad}$ is the horizontal incident x-ray beam divergence for our operating conditions. When $L \gg d$, the sample thickness can be ignored. As $L$ increases, the difference between $\theta_2$ and $\theta_1$ becomes smaller, thereby reducing $\Delta q$. Similarly, reducing the aperture size also decreases $\Delta q$, however, the downside is a reduction in the count rate. At larger $q$ values the thickness has a major effect on the value of $\Delta q$—doubling the thickness nearly doubles $\Delta q$ for $q > 50 \, \text{nm}^{-1}$.

Figure 3.17 is showing the momentum transfer as function of $\Delta q$. Notice how $\Delta q$ increases at higher momentum transfers for the three different annular slit sizes. The black dashed
Figure 3.17: Plot of $q$ values versus $\Delta q$ for the three different annular slit widths 1.0 mm (red line), 0.5 mm (green line), and 0.2 mm (blue line) using a sample thickness of $d = 3$ mm. The black dashed line represents $q = 14.25\,\text{nm}^{-1}$ and the color dashed lines are $\Delta q_{\text{red}} = \pm 2.7\,\text{nm}^{-1}$, $\Delta q_{\text{green}} = \pm 1.7\,\text{nm}^{-1}$, and $\Delta q_{\text{blue}} = \pm 1.2\,\text{nm}^{-1}$ for the associated annular slit.

The black dashed line at $q = 14.25\,\text{nm}^{-1}$ is where the peak of the structure factor for glycerol lies. Using a glycerol sample thickness of 3 mm will give $\Delta q = \pm 2.7\,\text{nm}^{-1}$ for a 1.0 mm annular slit, $\Delta q = \pm 1.7\,\text{nm}^{-1}$ for a 0.5 mm annular slit, and $\Delta q = \pm 1.2\,\text{nm}^{-1}$ for a 0.2 mm annular slit.

### 3.4.1.1 Effect on $\Delta q$ for sample to slit distance

Figure 3.18 describes how $\Delta q$ varies as a function of distance for the three different aperture sizes, assuming a sample thickness of $d = 3$ mm. Due to the method in which the annular slits were fashioned, with the outer diameter constant at 9 mm, the distance between the sample and annular slit slightly varies for the same $q$ value. For $q = 14\,\text{nm}^{-1}$,
the 1.0 mm annular slit has \( L = 20.6 \) mm, the 0.5 mm annular slit has \( L = 21.9 \) mm, and
the 0.2 mm annular slit has \( L = 22.6 \) mm, shown in Figure 3.18. For the 1.0 mm annular
slit \( \Delta q_{1.0} = \pm 2.7 \) nm\(^{-1}\), for the 0.5 mm annular slit \( \Delta q_{0.5} = \pm 1.7 \) nm\(^{-1}\), and for the 0.2 mm
annular slit \( \Delta q_{0.2} = \pm 1.2 \) nm\(^{-1}\). The figure also shows at small momentum transfers (below
5 nm\(^{-1}\)), or large \( L \) (above 60 mm), \( \Delta q \) is small regardless of the annular slit width.

Figure 3.18: The dependence of \( q \) and \( \Delta q \) as function of distance. The solid line represents
\( q \)-values from Equation (3.1) assuming a sample width of \( d = 3 \) mm. The shaded region
represents \( \Delta q \) accounting for the aperture sizes of (a) 1.0 mm, (b) 0.5 mm, and (c) 0.2 mm.
At \( q = 14 \) nm\(^{-1}\) the resolution worsens the wider the annular slit, as shown in the three
figures. To reduce the resolution one can resort to narrower annular slits widths albeit at
reduced data collection rate.

### 3.4.1.2 Sample thickness

The sample thickness also contributes to \( \Delta q \), as seen in Figure 3.19. Going from left
to the right, the figure shows what happens as the sample thickness increases. The solid
line shows \( q \)-values from Equation (3.1) and the shaded region shows \( \Delta q \) for three aperture
sizes of 0.2 mm (top row), 0.5 mm (middle row), and 1.0 mm (bottom row). Table 3.1 gives
\( \Delta q \) for a 1.0 mm, 0.5 mm, and 0.2 mm annular slits and at momentum transfers \( q = 50, 14, \)
and 5 nm\(^{-1}\) for sample thicknesses ranging from 0 to 10 mm. The table shows that at high
momentum transfers (\( q = 50 \) nm\(^{-1}\) and \( L \approx 5 \) mm), the sample thickness has a greater effect.
on $\Delta q$. Compared to low momentum transfers ($q = 5 \text{ nm}^{-1}$ and $L \approx 60 \text{ mm}$), the sample thickness has very little effect on $\Delta q$.

Figure 3.19: The dependence of $q$ and $\Delta q$ as function of sample thickness. The solid line represents $q$-values from Equation (3.1) for the different sample thicknesses. The shaded region represents $\Delta q$ accounting for the aperture sizes of 0.2 mm (top row), 0.5 mm (middle row), and 1.0 mm (bottom row) at those sample thicknesses.

Table 3.1: Tabulated values of $\Delta q$ for the 1.0 mm, 0.5 mm, and 0.2 mm slits and momentum transfers of $q = 50, 14$, and $5 \text{ nm}^{-1}$ as function of sample thickness.
3.4.1.3 Annular slit size

When deciding the size of the slit, there is a trade-off between the \( q \)-resolution and count rate. A large slit increases the count rate at the cost of \( q \)-resolution, and a small slit increases the resolution at the expense of lower count rates. Table 3.2 shows \( \Delta q \) for different slit sizes at momentum transfers \( q = 50, 14, \) and \( 5 \) \( \text{nm}^{-1} \) for a sample thickness of \( d = 3 \) mm. The table shows that the smaller the slit size the better the \( q \)-resolution.

Table 3.2: Tabulated values of \( \Delta q \) for the different slit widths at momentum transfers of \( q = 50, 14, \) and \( 5 \) \( \text{nm}^{-1} \) for sample thickness of \( d = 3 \) mm.

<table>
<thead>
<tr>
<th>Annular Slit Size (mm)</th>
<th>( q = 50 ) ( \text{nm}^{-1} )</th>
<th>( q = 14 ) ( \text{nm}^{-1} )</th>
<th>( q = 5 ) ( \text{nm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>( \pm 10 )</td>
<td>( \pm 1.0 )</td>
<td>( \pm 0.17 )</td>
</tr>
<tr>
<td>0.2</td>
<td>( \pm 11 )</td>
<td>( \pm 1.2 )</td>
<td>( \pm 0.23 )</td>
</tr>
<tr>
<td>0.3</td>
<td>( \pm 11 )</td>
<td>( \pm 1.4 )</td>
<td>( \pm 0.29 )</td>
</tr>
<tr>
<td>0.4</td>
<td>( \pm 12 )</td>
<td>( \pm 1.6 )</td>
<td>( \pm 0.35 )</td>
</tr>
<tr>
<td>0.5</td>
<td>( \pm 12 )</td>
<td>( \pm 1.7 )</td>
<td>( \pm 0.4 )</td>
</tr>
<tr>
<td>0.6</td>
<td>( \pm 13 )</td>
<td>( \pm 1.9 )</td>
<td>( \pm 0.5 )</td>
</tr>
<tr>
<td>0.7</td>
<td>( \pm 13 )</td>
<td>( \pm 2.1 )</td>
<td>( \pm 0.5 )</td>
</tr>
<tr>
<td>0.8</td>
<td>( \pm 14 )</td>
<td>( \pm 2.3 )</td>
<td>( \pm 0.6 )</td>
</tr>
<tr>
<td>0.9</td>
<td>( \pm 14 )</td>
<td>( \pm 2.5 )</td>
<td>( \pm 0.7 )</td>
</tr>
<tr>
<td>1.0</td>
<td>( \pm 15 )</td>
<td>( \pm 2.7 )</td>
<td>( \pm 0.8 )</td>
</tr>
<tr>
<td>1.25</td>
<td>( \pm 16 )</td>
<td>( \pm 3.2 )</td>
<td>( \pm 0.9 )</td>
</tr>
<tr>
<td>1.5</td>
<td>( \pm 18 )</td>
<td>( \pm 4 )</td>
<td>( \pm 1.1 )</td>
</tr>
<tr>
<td>1.75</td>
<td>( \pm 19 )</td>
<td>( \pm 4 )</td>
<td>( \pm 1.3 )</td>
</tr>
<tr>
<td>2.0</td>
<td>( \pm 21 )</td>
<td>( \pm 5 )</td>
<td>( \pm 1.6 )</td>
</tr>
</tbody>
</table>

Choosing the two different slit widths (1.0 mm and 0.5 mm) came down to a compromise between \( q \)-resolution and count rate. Using Equation (3.3) with a sample thickness of 3 mm gives \( \Delta q = \pm 2.7 \) \( \text{nm}^{-1} \) for 1.0 mm and \( \Delta q = \pm 1.7 \) \( \text{nm}^{-1} \) for 0.5 mm annular slits at \( q = 14.25 \) \( \text{nm}^{-1} \). This increases the count rate, because we are collecting the entire scattering annulus, by several factors making the measurements possible even at low \( q \) values. Table 3.3 shows data for different momentum transfers and annular slit sizes at room temperature for
glycerol. Using the annular slits increased our count rate by about two orders of magnitude at $q = 14.25 \text{nm}^{-1}$. This, in turn, enables measurements at $q$-values previously unexplored.

Table 3.3: The counting rates and relaxation times for multiple $q \pm \Delta q$ for different slit sizes at $T = 300 \text{K}$ for pure glycerol.

<table>
<thead>
<tr>
<th>Slit Size (mm)</th>
<th>Momentum Transfer (nm$^{-1}$)</th>
<th>Count Rate (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.9 ± 0.3</td>
<td>1.76</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0 ± 0.4</td>
<td>8.19</td>
</tr>
<tr>
<td>0.5</td>
<td>6.9 ± 0.6</td>
<td>14.7</td>
</tr>
<tr>
<td>0.5</td>
<td>10.0 ± 1.1</td>
<td>53.2</td>
</tr>
<tr>
<td>1.0</td>
<td>14.0 ± 2.7</td>
<td>106.6</td>
</tr>
<tr>
<td>1.0</td>
<td>20 ± 4</td>
<td>13.9</td>
</tr>
</tbody>
</table>

### 3.5 Glycerol

The sample was pure glycerol ($\text{CH}_2\text{OH}−\text{CHOH}−\text{CH}_2\text{OH}$)—it is a colorless and odorless liquid. Glycerol is a well-studied material that has relaxation times in the range of NR-TDI measurements (1 to 7000 ns). The size of a glycerol molecule is approximately $(0.48 \times 0.51 \times 0.78) \text{nm}$[28]. The density of glycerol is $1.261 \text{g cm}^{-3}$, the melting point is $T_m = 290.0 \text{K}$, and the glass transition temperature is $T_g \approx 190 \text{K}$.[44–47] The viscosity of glycerol at $20^\circ\text{C}$ is $\eta = 1.412 \text{Pa s}$. 
3.6 Sample Holder

The glycerol was held in custom sample holders and over the course of the experiment three different versions were implemented. The first two holders were similar in shape, but with different volumes for the sample, see Figure 3.21(a) and Figure 3.21(b). The sample holders were approximately $20 \text{mm} \times 20 \text{mm} \times 6 \text{mm}$ shaped like a wedge so that the sample thickness could be varied. Kapton tape covered the slot with the liquid sample inside and epoxy was used to seal the liquid inside. This was not a great method for holding liquids in general under vacuum, but for a high viscous sample (like glycerol) it was suitable. For less
viscous materials (like water), extra care was needed to prevent the sample from leaking. This led to the current sample holder, Figure 3.21(c), which uses three Kapton capillaries. These capillaries are sealable and did not leak under vacuum. The drawback is the sample thickness cannot be varied. However, tested with glycerol the 2 mm capillary had suitable count rates.

(a) Aluminum sample holder with a sample volume of 250 mm$^3$ used to hold a liquid sample.
(b) Copper sample holder with a sample volume of 50 mm$^3$ used to hold a liquid sample.
(c) Copper sample holder using three 2 mm diameter capillary tubes with an approximate volume of 30 mm$^3$ used to hold a liquid samples.

Figure 3.21: Versions of the sample holders used to hold the liquid glycerol sample.

Three silicon temperature diodes were used to measure the temperature of the sample. One diode was attached to cryostat’s cold head, another diode attached to the cold finger, and the last diode was attached directly to the sample holder, see Figure 3.22. The temperature sensors were periodically calibrated using ice water and liquid nitrogen. A resistive cartridge heater was used to control the temperature with temperature stability of ±0.1 K.
Figure 3.22: Cryostat setup including the cold head, cold finger, and the two different sample holders.
CHAPTER 4
RESULTS

4.1 The Dynamic Intermediate Scattering Function

The equation below, Equation (2.70), represents the intensity of the scattered x-rays including the diffusional motion of a liquid sample and combination of $^{57}\alpha$Fe and SS foils at a finite $q$:

\[
I(q, t) = 2 \left| G_{Fe}(t) \right|^2 \left( 1 + \cos \left[ \Omega t \right] \right) + f_{\Delta \kappa}(q) \left| G_{SS}(t) \right|^2 + 4G_{Fe}(t)G_{SS}(t) f_q e^{-\left( \frac{t}{\tau_K} \right)^\beta} \cos \left[ \frac{\Omega}{2} t \right] \cos [\omega_{IS} t]
\]

where the intermediate scattering function for glycerol can be modeled by the Kohlrausch–Williams–Watts (KWW)[24] stretched exponential as

\[
\frac{F(q, t)}{F(q, 0)} = f_q e^{-\left( \frac{t}{\tau_K} \right)^\beta} \quad \text{with } 0 < \beta < 1.
\]

One could also consider a two-step relaxation function to describe a modified intermediate scattering function consisting of both a fast exponential decay and a slow stretched exponential decay.[49]

\[
\frac{F'(q, t)}{F(q, 0)} = (1 - f_q) e^{-\left( \frac{t}{\tau_1} \right)} + f_q e^{-\left( \frac{t}{\tau_2} \right)^\beta}
\]

(4.1)

where $\tau_1$ is the fast decay and $\tau_2$ is the slow decay, $beta$ is the stretching exponent, and $f_q$ is the nonergodicity parameter. This thesis only considers the slow decays.
4.1.1 Fitting parameters

There are four fitting parameters for the intermediate scattering function: the electronic absorption factor $f_{ΔE}$, non-ergodicity factor $f_q$, stretching exponent $β$, and relaxation time $τ_K$. Determining how these fitting parameters affects the outcome of the relaxation time is key to understanding the molecular dynamics of a liquid sample. Figure 4.1 is a simulation with the same fitting parameters at various relaxation times showing how the peaks and troughs vary as function of time. The fits used Equation (2.70) and the values in Table 2.2 for $T_{Fe}$, $T_{SS}$, $Ω$, and $ω_{IS}$ with $f_{ΔE} = 1$, $f_{q} = 1$, and $β = 0.6$. Notice the relaxation times below 10 ns and above 10,000 ns are difficult to distinguish because of the overlapping lines at the peaks and troughs for the different relaxation times, this limits the measurable relaxation times (see Section 4.2).

4.1.1.1 Electronic absorption factor $f_{ΔE}$

The electronic absorption factor, $f_{ΔE}$, is a fitting parameter which aids in fitting how to best fit the peaks and troughs of the wave pattern and the width of each data set. Figure 4.2 shows two simulations for Equation (2.70) using the fitting parameters in Table 2.2 at two different relaxation times, Figure 4.2(a) shows $τ_K = 1$ ns, $f_q = 1$, and $f_{ΔE} = 1.00, 0.75, 0.50, and 0.25$ and Figure 4.2(b) shows simulation for $τ_K = 1000$ ns, $f_q = 1$, and $f_{ΔE} = 1.00, 0.75, 0.50, and 0.25$. The electronic absorption factor is a fractional scattering amplitude interfering with the SS foil, which increases the depth of the trough for decreasing $f_{ΔE}$ values. This parameter is acting like a damping function. Figure 4.3 shows the calculated fitting parameters for $f_{ΔE}$ as a function of temperature from the data collected at the APS. The data from the TDI measurement is shown in Table 4.1 and Figure 4.3. The median value
Figure 4.1: Simulated normalized intensities for various relaxation times. The experimental measurement window is between the red shaded regions (20 to 110 ns). The inset shows the second measurable peak from the data.

of the electronic absorption factor is $f_{\Delta E} = 0.69$ (the light red dashed line) across all the temperatures at $q = 14 \text{ nm}^{-1}$. The gray shaded region in Figure 4.2 shows the span of $f_{\Delta E}$ values ($0.61 < f_{\Delta E} < 0.75$) and the black dashed curve is for average value ($f_{\Delta E} = 0.69$). Over this span ($f_{\Delta E}$) does not play a major role when determining the outcome of the relaxation times.
Figure 4.2: Simulated normalized intensities for different \( f_{\Delta E} \) values for different relaxation times (\( \tau_K = 1 \text{ ns} \) and 1000 ns). The light gray shaded region is the range between the maximum and minimum electronic absorption factors (0.61 < \( f_{\Delta E} < 0.75 \)) from the experimental data and the dashed black curve is the average absorption factor (\( f_{\Delta E} = 0.69 \)). The light red shaded region is outside the measurement window used for NR-TDI (between 20 to 115 ns). The insets are zooming in at the contrast peaks on a time scale between 35 ns and 51 ns.

Figure 4.3: Fitted data for \( f_{\Delta E} \) for pure glycerol. The red dashed line is mean value for all the electronic absorption factors, \( f_{\Delta E} = 0.69 \).
Table 4.1: List of $f_{\Delta E}$ as function of temperature for pure glycerol.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$f_{\Delta E}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.66 ± 0.01</td>
</tr>
<tr>
<td>195</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>200</td>
<td>0.72 ± 0.01</td>
</tr>
<tr>
<td>202</td>
<td>0.71 ± 0.01</td>
</tr>
<tr>
<td>204</td>
<td>0.75 ± 0.01</td>
</tr>
<tr>
<td>206</td>
<td>0.71 ± 0.01</td>
</tr>
<tr>
<td>208</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>210</td>
<td>0.72 ± 0.02</td>
</tr>
<tr>
<td>215</td>
<td>0.71 ± 0.01</td>
</tr>
<tr>
<td>220</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>225</td>
<td>0.69 ± 0.01</td>
</tr>
<tr>
<td>226</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>228</td>
<td>0.67 ± 0.01</td>
</tr>
<tr>
<td>230</td>
<td>0.67 ± 0.01</td>
</tr>
<tr>
<td>232</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>234</td>
<td>0.68 ± 0.01</td>
</tr>
<tr>
<td>250</td>
<td>0.70 ± 0.01</td>
</tr>
<tr>
<td>263</td>
<td>0.69 ± 0.01</td>
</tr>
<tr>
<td>276</td>
<td>0.68 ± 0.02</td>
</tr>
<tr>
<td>300</td>
<td>0.61 ± 0.01</td>
</tr>
<tr>
<td>Midrange</td>
<td>0.68 ± 0.07</td>
</tr>
</tbody>
</table>
4.1.1.2 Non-ergodicity factor, $f_q$

The non-ergodicity factor is highly coupled with the relaxation time and because it is sensitive to the dynamics of the sample, defining an appropriate value is essential for calculating the relaxation times. Ergodicity is the idea that for a specific point, like an atom or molecule in a dynamical system, the point is freely able to move randomly around, eventually to all possible spaces. The opposite is true for non-ergodicity, where the molecule is locked in place or restricted in movement. If you consider a single particle freely moving within a system of particles, then the non-ergodicity factor should be close to zero.[35] Figure 4.4(a) shows the red particle freely able to move around in the system of blue particles because the system is in liquid form. This non-ergodicity factor, called $f_q$, is part of the intermediate scattering function and can destroy the coherence between the $\alpha^{57}$Fe and SS foils. Coherence between the foils is clearly evident by the Reissverschluss (zipper)[50] asymmetry in the amplitudes of the quantum beat pattern shown in Figure 4.5(c). When the coherence is lost this zipper pattern disappears as shown in Figure 4.5(a). The other factor that can destroy the coherence between the foils is a fast relaxation rate. Thus, small $\tau_K$ or small $f_q$ will make the third interference term in Equation (2.70) small.

Figure 4.5 shows the simulation of Equation (2.70) using the fitting parameters in Table 2.2 for $T_{Fe}$, $T_{SS}$, $\Omega$, and $\omega_{IS}$ at five different non-ergodicity values ($f_q = 1$, 0.75, 0.5, 0.25, and 0) and for five different relaxation times ($\tau_K = 1\text{ ns}$, 10 ns, 100 ns, 1000 ns, and $\infty$). Notice that all five plots have the same identical curves when $f_q = 0$. This is because the non-ergodicity factor multiplies the third term in Equation (2.70) by zero, which eliminates that term. From the mode coupling theory, $f_q = 0$ corresponds to the sample being in a liquid state and free to move around without any restrictions. This is exactly what is seen in the simulation.
(a) Depiction of molecule in the liquid phase, the red molecule can move freely around the surrounding molecules because the $f_q \approx 0$ indicating the sample is in a liquid state. Compared to a glassy state which would not allow the red molecules to flow freely around the neighboring molecule because the $f_q \approx 1$.[35]

(b) The red particle is “caged-in” by the surrounding blue particles indicated by the dashed circular line. The red particle can only move as a unit of both red and blue particles making it much more difficult to freely move around, this causes the relaxation times to slow down because the $f_q > 0$ indicating the sample is in a supercooled or solid state.

Figure 4.4: Mode-Coupling Theory (MCT) of glass and liquid transitions.

When the sample is cooled to a supercool state the molecules get closer together thereby restricting their movement. As seen in Figure 4.4(b), the red particle becomes “caged-in” by the surrounding particles inside the dashed circle. Now the only thing that can move is a cluster of particles since each individual particle is “caged-in”. The cluster of particles must move as one entire unit. In the glassy state, it is more difficult for this unit to move freely, thereby slowing down the relaxation time.

Figures 4.5(a) and (b) show the results for fast relaxation rates when the sample is essentially in a liquid state ($\tau_K = 1\, \text{ns}$ and $\tau_K = 10\, \text{ns}$). Figure 4.5(c) and (d) show the results for slower relaxation rates caused by cooling the sample into a glassy state ($\tau_K = 100\, \text{ns}$ and $\tau_K = 1000\, \text{ns}$). Figure 4.5(e) shows the result with the sample cooled to a solid state ($\tau_K = \infty$).
Figure 4.5: Simulated normalized intensities for different $f_q$ values and relaxation times. The light red shaded region is outside the measurement window used for NR-TDI (between 20 to 115 ns). The insets are zooming in at the contrast peaks on a time scale between 35 ns and 51 ns. The light gray shaded region is the range between the maximum and minimum $f_q$ values ($0.57 < f_q < 0.65$) from the experimental data.
Figure 4.6: Experimental data for $f_q$ as a function of temperature for pure glycerol. The dashed curve is a linear fit using the values below 240 K. The green data points are extrapolated values used for temperatures above 240 K.

Figure 4.6 shows experimental data (red circles) for non-ergodicity factor values, $f_q$, as a function of temperature for data taken during the January 2021 experiment run. As the sample changes from glassy state to a liquid state, there was strong coupling between the fitting parameters $f_q$ and $\tau_K$. Allowing $f_q$ to vary during these fits caused the sharp drop in these values for temperatures above 240 K (while $\tau_K$ increased significantly), as shown in Figure 4.6. To avoid unphysically large values of $\tau_K$ in the glassy region, $f_q$ was fixed to lie along a line extrapolated from fitted values of $f_q$ below 240 K. These values are shown as the green squares in Figure 4.6.
Table 4.2: List of $f_q$ as function of temperature for pure glycerol. The $f_q$ values above 240 K were found from a linear equation using the data between 160 K and 240 K.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$f_q$ (free)</th>
<th>$f_q$ (fixed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.65 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>195</td>
<td>0.65 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.65 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>202</td>
<td>0.63 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>204</td>
<td>0.61 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>206</td>
<td>0.62 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>208</td>
<td>0.60 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>0.62 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>215</td>
<td>0.63 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>0.60 ± 0.02</td>
<td></td>
</tr>
<tr>
<td>225</td>
<td>0.67 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>226</td>
<td>0.60 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>228</td>
<td>0.65 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>0.61 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>0.62 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>234</td>
<td>0.62 ± 0.04</td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.29 ± 0.06</td>
<td>0.606415</td>
</tr>
<tr>
<td>263</td>
<td>0.074 ± 0.003</td>
<td>0.598826</td>
</tr>
<tr>
<td>276</td>
<td>0.060 ± 0.004</td>
<td>0.591237</td>
</tr>
<tr>
<td>300</td>
<td>0.088 ± 0.003</td>
<td>0.577227</td>
</tr>
</tbody>
</table>

### 4.1.1.3 Stretching Exponent, $\beta$

The stretching exponent is a fixed fitting parameter at $\beta = 0.6$. When studying the relaxation of glasses using the “trapping model” where the sample is filled with randomly distributed traps. The molecules or atoms want to fill these traps and the model predicts

$$
\beta = \frac{d}{d+2}.
$$

(4.2)
where $d$ is the dimensions.[27] In the case of three dimension ($d = 3$) the trapping model gives a value of $\beta = 0.6$. It is also difficult to fit this parameter and most papers use a range of values $0.6 < \beta < 0.7$, therefore fixing $\beta = 0.6$ seems reasonable.[6, 10, 25]

Figure 4.7 shows the simulation of Equation (2.70) using the fitting parameters in Table 2.2 for $T_{Fe}$, $T_{SS}$, $\Omega$, and $\omega_{IS}$ at five different $\beta$ values ($\beta = 1, 0.75, 0.6, 0.5, \text{and} 0.25$) and four different relaxation times ($\tau_K = 1 \text{ ns,} 10 \text{ ns,} 100 \text{ ns, and} 1000 \text{ ns}$). Notice there is little difference between the peaks and troughs at the different $\beta$ values, therefore having little effect on the calculated relaxation times.

![Simulation Diagram](image)

Figure 4.7: Simulated normalized intensities for different $\beta$ values and relaxation times. The light red shaded region is outside the measurement window used for NR-TDI (between 20 to 115 ns).
4.2 Measurable relaxation times limitation

The sensitivity of the NR-TDI technique for measuring the relaxation time can be determined by the degree of modulation of the time spectra. This is shown in Figure 4.8 where the gray shaded modulation region shows how the time spectrum evolves from a short relaxation time (solid red curve) to the heavily modulated spectrum having a long relaxation time (solid blue curve). The figure shows the simulations which are all normalized to unity at time $t = 0$. The gray shaded region covers the series of measurements given in Table 4.3 for the 1.0 mm annular slit. From the degree of modulation of the spectra, it appears to be possible to measure relaxation times over a large dynamic range covering 4 orders of magnitude from 1 ns to at least 10,000 ns (as shown in Figure 1.1).

The log of the intensity, at $t = 42.5$ ns in Figure 4.8, as a function of relaxation time is the red curve shown in Figure 4.9(a). The log of the intensity curve was adjusted so that it is 1 at $t = 0$ and 0 at $t = \infty$. The solid blue circles are from the 20 measurements given in Table 4.3 for pure glycerol. The curve plateaus for times less than 1 ns and greater than 100,000 ns showing that experiments are not very sensitive to measuring relaxation times near those regions. The normalized contrast curve in Figure 4.9(b) is the derivative of the red curve, $d(\log \text{Intensity}) / d(\log \tau_K)$, showing that the peak sensitivity for this particular NR-TDI technique lies around 100 ns. When the error bars of the relaxation times are greater than 10\%, the contrast value falls below 15\%, indicating the limitation of reliable measurements. For a 15\% contrast the sensitivity ranges from 5 ns to 20,000 ns is shown by the dashed line in Figure 4.9(b).[51]
Figure 4.8: Normalized intensities for various relaxation times. The gray shaded region spans the measurements done in Table 4.3. The curves outside the gray shaded region are theoretical calculations for relaxation times and the measurement window is between the red shaded regions (20 to 110 ns).
Figure 4.9: Sensitivity curves for NR-TDI measurements using pure glycerol where the smooth curves are simulations and the solid circles are evaluations at the values of $\tau_K$ given in Table 4.3 (a) log intensity at $t = 42.5$ ns in Figure 4.8, (b) the contrast is the derivative of the curve in (a).
Table 4.3: Table of relaxation times at multiple temperatures for pure glycerol using 1.0 mm annular slit at 14 nm\(^{-1}\) corresponding to the average inter-molecular distance of glycerol. The mean relaxation time can be calculated using the formula \(\langle \tau \rangle = \frac{\tau}{\beta} \Gamma \left(\frac{1}{\beta}\right) \approx 1.5\tau\) (\(\beta\) was fixed to 0.6 for all fits).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(\tau_K) (ns)</th>
<th>(\langle \tau_K \rangle) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>((1.61 \pm 0.29) \times 10^4)</td>
<td>((2.4 \pm 0.4) \times 10^4)</td>
</tr>
<tr>
<td>195</td>
<td>((1.63 \pm 0.35) \times 10^4)</td>
<td>((2.5 \pm 0.5) \times 10^4)</td>
</tr>
<tr>
<td>200</td>
<td>5185 \pm 556</td>
<td>7802 \pm 837</td>
</tr>
<tr>
<td>202</td>
<td>((7.5 \pm 1.1) \times 10^3)</td>
<td>((1.12 \pm 0.17) \times 10^4)</td>
</tr>
<tr>
<td>204</td>
<td>((7 \pm 4) \times 10^4)</td>
<td>((1.1 \pm 0.6) \times 10^5)</td>
</tr>
<tr>
<td>206</td>
<td>((1.10 \pm 0.20) \times 10^4)</td>
<td>((1.66 \pm 0.30) \times 10^4)</td>
</tr>
<tr>
<td>208</td>
<td>((3.1 \pm 1.0) \times 10^4)</td>
<td>((4.7 \pm 1.5) \times 10^4)</td>
</tr>
<tr>
<td>210</td>
<td>5802 \pm 775</td>
<td>((8.7 \pm 1.2) \times 10^3)</td>
</tr>
<tr>
<td>215</td>
<td>3234 \pm 296</td>
<td>4866 \pm 445</td>
</tr>
<tr>
<td>220</td>
<td>3436 \pm 338</td>
<td>5170 \pm 509</td>
</tr>
<tr>
<td>225</td>
<td>463 \pm 12</td>
<td>697 \pm 19</td>
</tr>
<tr>
<td>226</td>
<td>780 \pm 33</td>
<td>1174 \pm 49</td>
</tr>
<tr>
<td>228</td>
<td>336 \pm 9</td>
<td>505 \pm 13</td>
</tr>
<tr>
<td>230</td>
<td>323 \pm 7</td>
<td>485 \pm 11</td>
</tr>
<tr>
<td>232</td>
<td>232 \pm 6</td>
<td>348 \pm 9</td>
</tr>
<tr>
<td>234</td>
<td>174 \pm 4</td>
<td>262 \pm 6</td>
</tr>
<tr>
<td>250</td>
<td>80 \pm 4</td>
<td>120 \pm 6</td>
</tr>
<tr>
<td>263</td>
<td>15.5 \pm 0.6</td>
<td>23.3 \pm 0.9</td>
</tr>
<tr>
<td>276</td>
<td>13.1 \pm 0.6</td>
<td>19.8 \pm 0.9</td>
</tr>
<tr>
<td>300</td>
<td>18.5 \pm 0.7</td>
<td>27.9 \pm 1.0</td>
</tr>
</tbody>
</table>
4.3 Pure Glycerol Sample

TDI measurements are notoriously difficult to perform using either radioactive sources or synchrotron x-rays due to low count rates. This is because the intensity of the quasielastic scattered photons is 5 to 6 orders of magnitude lower than the direct beam. To overcome this problem, we developed a new optical component: an annular slit. The annular slit allows for the collection of all scattered photons for a particular momentum transfer using only one APD detector. This improvement, in turn, allows systematic studies of relaxation times over a range of momentum transfers and temperatures, and it presents an advantage over previous approaches [6, 10, 25].

Attaching an annular slit to an APD detector, as shown in Figure 3.14(b), allows for a much higher count rate and detection efficiency. For instance, using a detector with a 1.0 mm annular slit, Figure 3.15(a), has an average delayed count rate of 90 Hz at $q = 14 \text{nm}^{-1}$ and $T = 300 \text{K}$ for glycerol. Using the single detector setup shown in Figure 3.13, we measured an average delayed counting rate of 0.5 Hz for the same momentum transfer and temperature. However, the 1.0 mm annular slit has a $q$-resolution of $\pm 2.7 \text{nm}^{-1}$ compared to $\pm 0.5 \text{nm}^{-1}$ resolution for the single detector setup shown in Figure 3.13 (since the single detector was placed much further from the glycerol sample). With annular slits, it was possible to collect data at low $q$-values where the scattering intensity is naturally lower than the peak intensity of $S(q)$ (Figure 3.12). Table 4.4 lists the counting rates and relaxation times for multiple $q$-values and slit sizes at $T = 300 \text{K}$ for the pure glycerol sample. These counting rates make it possible to do measurements at momentum transfers as low as 1.88 nm$^{-1}$ and as high as 30 nm$^{-1}$.
4.3.1 Relaxation times as a function of momentum transfers

Table 4.4: The counting rates and relaxation times for multiple \( q \)-values and slit sizes at \( T = 300 \text{ K} \) for pure glycerol. The mean relaxation time can be calculated using the formula \( \langle \tau \rangle = \frac{\tau}{\beta} \Gamma \left( \frac{1}{\beta} \right) \approx 1.5\tau \) (\( \beta \) was fixed to 0.6 for all fits).

<table>
<thead>
<tr>
<th>Slit Size (mm)</th>
<th>Momentum Transfer (nm(^{-1}))</th>
<th>Count Rate (Hz)</th>
<th>( \tau_K ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>1.88 ± 0.3</td>
<td>1.76</td>
<td>1999 ± 650</td>
</tr>
<tr>
<td>0.5</td>
<td>5.0 ± 0.4</td>
<td>8.19</td>
<td>1004 ± 115</td>
</tr>
<tr>
<td>0.5</td>
<td>6.9 ± 0.6</td>
<td>14.7</td>
<td>317 ± 32</td>
</tr>
<tr>
<td>0.5</td>
<td>10.0 ± 1.1</td>
<td>53.2</td>
<td>25.8 ± 1.2</td>
</tr>
<tr>
<td>1.0</td>
<td>14.0 ± 2.7</td>
<td>106.6</td>
<td>18.5 ± 0.7</td>
</tr>
<tr>
<td>1.0</td>
<td>20 ± 4</td>
<td>13.9</td>
<td>5.4 ± 0.2</td>
</tr>
</tbody>
</table>

The dynamic intermediate scattering function given by Equation (2.45) determines the degree of coherence as measured by the time domain interferometer. The KWW stretched exponential function contains information about fluctuations in the electron density from the sample due to the dynamic diffusional motion of its molecules. The relaxation time \( \tau_K \) is function of both temperature and momentum transfer and found by fitting the quantum beat spectra to Equation (2.70).

The dramatic change in the time spectra as \( q \) is varied from 1.88\,\text{nm}^{-1} \) to 20\,\text{nm}^{-1} \) in Figure 4.10 at \( T = 300 \text{ K} \) is showing the \( q \) dependence on \( \tau_K \). The momentum transfer is inversely related to distance, where when \( q \) is small we are zooming out and viewing the entire glycerol molecule having a slower relaxation rate (\( \tau_K = 2000 \text{ ns} \)). When \( q \) is bigger we are zooming in and viewing individual atoms inside the molecule have a faster relaxation rate (\( \tau_K = 5 \text{ ns} \)).

When \( q = 14 \text{ nm}^{-1} \), a spectrum was measured having a relaxation time of 18.5 ± 0.7\,\text{ns}. For such a short relaxation time, the KWW function is small (\( \frac{F(q,t)}{F(q,0)} = 0.03 \) when averaged over times between 0 and 153\,\text{ns} \) which in turn makes the coherence term in Equation (2.70)
Figure 4.10: NR-TDI results for pure glycerol at 300 K at four different momentum transfers (a) \( q = 20 \text{ nm}^{-1} \), (b) \( q = 14 \text{ nm}^{-1} \), (c) \( q = 5 \text{ nm}^{-1} \), and (d) \( q = 1.88 \text{ nm}^{-1} \). Blue dots: experimental data. Red solid line: fit obtained using Equation (2.70). The green lines above the plots are the respective residuals for the fits.

(The third term) small. Thus, the coherence between the Fe and SS foils has been greatly reduced resulting in the spectrum shown in Figure 4.10(b). At smaller \( q \), the KWW function becomes larger for glycerol which in turn makes the coherence term in Equation (2.70) larger. This result is seen by the significantly modulated spectrum shown in Figure 4.10(d) for \( q = 1.88 \text{ nm}^{-1} \) at the same temperature. This spectrum has a much longer relaxation time of \( 1999 \pm 650 \text{ ns} \) resulting in the KWW function being larger \( \frac{F(q,t)}{F(q,0)} = 0.51 \) when averaged over times between 0 and 153 ns). The zipper beat pattern is more pronounced at longer
relaxation times. This indicates that there is a reduction in the diffusional motion of the glycerol molecules, and thus maximizes the interference between the Fe and SS foils.

Figure 4.11 shows a plot of relaxation times as a function of momentum transfers for the two different aperture sizes. The $q$-resolution improves at lower momentum transfers because the detector is placed further from the sample in order for the x-rays to make it through the annular slit. The benefit of using the wider aperture is a higher count rate, but there is a sacrifice in the $q$-resolution because the detector must be placed closer to the sample.

Figure 4.11: Calculated relaxation times using two different annular slits for pure glycerol at $q = 2, 5, 7, 10, 15,$ and $20$ nm$^{-1}$ at 300 K. The blue squares are for the 1.0 mm and the red circles are for the 0.5 mm slit widths.
4.3.2 Relaxation times \((\tau_\kappa)\) as a function of temperature \((T)\)

The previous section showed an increase in relaxation times for decreasing momentum transfers. Not only is the relaxation time a function of momentum transfer, but it is also a function of temperature. Figure 4.12 shows how SMS modulated spectra is significantly different at temperatures (a) \(T = 300\,\text{K}\), (b) \(T = 234\,\text{K}\), (c) \(T = 215\,\text{K}\), and (d) \(T = 190\,\text{K}\). The zipper beat pattern is more pronounced as the temperature decreases. This indicates that the liquid sample is changing to a supercooled state before freezing to a solid.

The relaxation times, \(\tau_\kappa\), obtained from the analysis of the quantum beat patterns collected between the temperature ranges (190 to 300 K) at \(q = 14\,\text{nm}^{-1}\) are plotted in Figure 4.13. For the pure glycerol sample used in this thesis, the glass transition temperature was estimated to be around 185 K which agrees reasonably well with differential scanning calorimetry (188.9 K).[47] At higher temperatures we can observe relaxation dynamics well before the melting point reported in the literature \((T_m = 291\,\text{K})\). There is a significant increase in the diffusive motion of glycerol molecules over a 40 K temperature span before the onset of melting where the material is in a soft glassy phase.[44–46] Included in Figure 4.13 for comparison are calculated values of relaxation times from Alfred Baron[6] and Makina Saito[25] for pure glycerol.

4.3.2.1 Mean relaxation time

The mean relaxation time,

\[
\langle \tau \rangle = \frac{\tau \Gamma \left( \frac{1}{\beta} \right)}{\beta},
\]

(4.3)
as a function of inverse temperature is shown in Figure 4.14. This data can be used to better understand the glass transition dynamics of liquid samples near the glass transition and supercooled regime. The NR-TDI measurements are sensitive to the Johari-Goldstein, $\beta_{JG}$, relaxation which can be used to find the glass transition, $T_g$. The $T_g$ is estimated by the change in the shape of the average relaxation plot. Where above the $T_g$ the shape is flatter and in the is the $\beta$-relaxation regime, compared to relaxation times below the $T_g$ where the shape is more quadratic and in the $\alpha$-relaxation regime.
In the $\beta$-relaxation zone the molecules are restricted from moving freely because of the “caging” effect occurring in the system of molecules, as seen in Figure 4.4(b). In this regime, the red molecule cannot move freely outside the neighboring molecules, instead the neighboring and central molecule move as group making translations more difficult thus increasing the viscous flow and increasing the relaxation times. In this zone the relaxation time plateaus with very little increase of relaxation times as the temperature continues to cool. Compared to the $\alpha$-relaxation zone, Figure 4.4(a), where the molecules move freely around one another and the relaxation rates increase. The dynamical scattering can be modeled by the KWW stretched exponential function. [35]
Table 4.5: List of fitting values for glycerol as function of temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( f_{\Delta E} )</th>
<th>( f_q )</th>
<th>( \tau_K ) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>0.66 ± 0.01</td>
<td>0.65 ± 0.02</td>
<td>(1.61 ± 0.29) \times 10^4</td>
</tr>
<tr>
<td>195</td>
<td>0.68 ± 0.01</td>
<td>0.65 ± 0.02</td>
<td>(1.63 ± 0.35) \times 10^4</td>
</tr>
<tr>
<td>200</td>
<td>0.72 ± 0.01</td>
<td>0.65 ± 0.02</td>
<td>5185. ± 556.</td>
</tr>
<tr>
<td>202</td>
<td>0.71 ± 0.01</td>
<td>0.63 ± 0.02</td>
<td>(7.5 ± 1.1) \times 10^3</td>
</tr>
<tr>
<td>204</td>
<td>0.75 ± 0.01</td>
<td>0.61 ± 0.02</td>
<td>(7 ± 4) \times 10^4</td>
</tr>
<tr>
<td>206</td>
<td>0.71 ± 0.01</td>
<td>0.62 ± 0.02</td>
<td>(1.10 ± 0.20) \times 10^4</td>
</tr>
<tr>
<td>208</td>
<td>0.70 ± 0.01</td>
<td>0.60 ± 0.02</td>
<td>(3.1 ± 1.0) \times 10^4</td>
</tr>
<tr>
<td>210</td>
<td>0.72 ± 0.01</td>
<td>0.62 ± 0.02</td>
<td>5802 ± 775</td>
</tr>
<tr>
<td>215</td>
<td>0.71 ± 0.01</td>
<td>0.63 ± 0.02</td>
<td>3234 ± 296</td>
</tr>
<tr>
<td>220</td>
<td>0.70 ± 0.01</td>
<td>0.60 ± 0.02</td>
<td>3436 ± 338</td>
</tr>
<tr>
<td>225</td>
<td>0.68 ± 0.01</td>
<td>0.67 ± 0.03</td>
<td>463 ± 12</td>
</tr>
<tr>
<td>226</td>
<td>0.68 ± 0.01</td>
<td>0.60 ± 0.03</td>
<td>780 ± 33</td>
</tr>
<tr>
<td>228</td>
<td>0.66 ± 0.01</td>
<td>0.65 ± 0.03</td>
<td>336 ± 9</td>
</tr>
<tr>
<td>230</td>
<td>0.67 ± 0.01</td>
<td>0.61 ± 0.02</td>
<td>323 ± 7</td>
</tr>
<tr>
<td>232</td>
<td>0.68 ± 0.01</td>
<td>0.62 ± 0.03</td>
<td>232 ± 6</td>
</tr>
<tr>
<td>234</td>
<td>0.68 ± 0.01</td>
<td>0.62 ± 0.04</td>
<td>174 ± 4</td>
</tr>
<tr>
<td>250</td>
<td>0.70 ± 0.01</td>
<td>0.61</td>
<td>80 ± 4</td>
</tr>
<tr>
<td>263</td>
<td>0.69 ± 0.01</td>
<td>0.60</td>
<td>15.5 ± 0.6</td>
</tr>
<tr>
<td>276</td>
<td>0.68 ± 0.02</td>
<td>0.59</td>
<td>13.1 ± 0.6</td>
</tr>
<tr>
<td>300</td>
<td>0.61 ± 0.01</td>
<td>0.58</td>
<td>18.5 ± 0.7</td>
</tr>
</tbody>
</table>

4.3.2.2 Intermediate scattering function

Figure 4.15 is the SMS data for pure glycerol at \( T = 300 \) K and \( q = 14 \text{ nm}^{-1} \) with a calculated relaxation time of \( \tau_K = 18.5 ± 0.7 \) ns. This beat pattern is very different than the beat pattern without any sample at same temperature in the forward direction, as seen in Figure 2.26. This shows that the sample dynamics destroys the coherence between the \( ^{57}\text{Fe} \) and SS foils, which is the third term in Equation (2.70). Recall the sample dynamics is found by the intermediate scattering function, Equation (2.45), which is

\[
\frac{F(q, t)}{F(q, 0)} = f_q e^{-\left(\frac{t}{\tau_K}\right)^\beta}.
\]
The average relaxation times as a function of temperature for (red circles using 1.0 mm annular slit) glycerol at the peak of the structure factor, $q = 14 \text{ nm}^{-1}$.

If this term goes to zero it corresponds to a sample in a liquid state.\textsuperscript{[35]}

The intermediate scattering function can go to zero by the following two options $f_q \to 0$ or $\tau_K \to 0$. At $T = 300 \text{ K}$ the relaxation time is found to be short ($\tau_K = 18.5 \pm 0.7 \text{ ns}$), therefore the exponential term approaches zero eliminating the coherence term. The green curve in Figure 4.15 is a simulation for a relaxation time $\tau_K = 0$. Similarly, one can also eliminate the coherence term when non-ergodicity term $f_q = 0$, which defines the sample as a liquid.

Figure 4.16 is the SMS data for pure glycerol at $T = 190 \text{ K}$ and $q = 14 \text{ nm}^{-1}$ with a relaxation time of $\tau_K = 16,100 \pm 2900 \text{ ns}$. This zipper beat pattern with pure glycerol is similar to the beat pattern without any sample in the forward direction, as seen in Figure...
Figure 4.15: SMS measurement at $q = 14\text{ nm}^{-1}$ at $T = 300\text{ K}$. The blue dots are data, the red curve is the fit giving ($\tau_K = 18.5\text{ ns}$), and the green curve is a simulated fit when $\tau_K = 0\text{ ns}$ or $f_q = 0$. Notice the red and green curves nearly completely overlaps.

2.26. This shows that the sample in the glassy state has little effect on the interference between the $^{57}\text{Fe}$ and SS foils.

When the sample is frozen the exponential term becomes one because of the large relaxation times, $\tau_K \rightarrow \infty$. From the data at $T = 190\text{ K}$, the calculated relaxation time is $\tau_K = 16,100 \pm 2900\text{ ns}$, therefore the exponential term approaches one, leaving only the non-ergodicity term in Equation (2.45). The green curve in Figure 4.16 is a simulation for a relaxation time $\tau_K = \infty$. 
Data Fit \( (\tau_K = (1.61 \pm 0.29) \times 10^4 \text{ ns}) \)

Simulation \( (\tau_K = \infty) \)

Figure 4.16: SMS measurement at \( q = 14 \text{ nm}^{-1} \) at \( T = 190 \text{ K} \). The blue dots are data, the red curve is the fit, and the green curve is a simulated fit when \( \tau_K = \infty \). Notice the red and green curves nearly completely overlaps.

4.3.3 Arrhenius equation

The ability to measure the relaxation times of a liquid sample at different temperatures and momentum transfers allows one to glean important information about the sample’s properties. As is the case for the glass transition, determining it has been a challenge for solid-state physics and material engineering for decades.\[52\] The Arrhenius equation is

\[
\tau_K(T) = \tau_0 \exp \left[ \frac{E_a}{RT} \right]
\]  \hspace{1cm} (4.4)

where \( E_a \) is the activation energy, \( R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \) is the universal gas constant, \( \tau_0 \) is the relaxation time at high temperature, and \( T \) is temperature. The activation energy
describes the energy barrier for molecular rearrangements from the liquid to solid phases. The slope of the Arrhenius equation,

\[ m = \frac{\text{d} \log_{10} \tau_k}{\text{d} \left( \frac{T_g}{T} \right)} \bigg|_{T=T_g}, \]  

(4.5)
gives what is called the “fragility” which is used to describe how the liquid sample dynamics is behaving around the glass transition. The slope \( m \) leads to glass forming liquid samples to be categorized as either “strong” \((m < 30)\) or “fragile” \((m > 30)\). According to the mode coupling theory, the fragility can be related to the intermediate scattering function describing the sample’s dynamics as a function of temperature and momentum transfer.

A glass is defined as a liquid that is no longer able to flow. The procedure by which glasses are obtained is by quickly reducing the temperature of the liquid below its glass transition temperature \((T_g)\). The rate of cooling should be fast enough that crystallization is avoided when crossing the melting temperature \((T_m)\). When a liquid is below \(T_m\), the liquid enters the supercooled state. As the temperature decreases the liquid passes from a liquid to a glassy state where the relaxation time increases by many orders of magnitude while the molecular dynamics slows down. The \(T_g\) is defined as the temperature when the relaxation dynamics of the molecules are on the timescale of \(10^{11}\) ns. This supercooled liquid becomes highly viscous and its ability to flow rapidly decreases when approaching \(T_g\).

Figure 4.17(a) shows the mean relaxation time as a function of temperature and Figure 4.17(b) shows the logarithmic mean relaxation time as a function of inverse temperature, where the red curve is a fit to the blue data points using the Arrhenius Equation (4.4). The gray data points are relaxation times not used in the fit. The calculated activation energy for glycerol was found to be 63.2 kJ mol\(^{-1}\) in Figure 4.17(a) (where the Arrhenius equation is used to fit the data) and 63.5 kJ mol\(^{-1}\) in Figure 4.17(b) (where the log of the Arrhenius equation is used to fit the data). Notice that these values are in close agreement with each
other. From the literature the activation energy for pure glycerol is 61 to 74 kJ mol\(^{-1}\).[57, 58] The data were fitted using a Levenberg-Marquardt routine, and \(\chi^2\) was calculated using

\[
\chi^2 = \sum_{i=1}^{N} \left( \frac{y_i - f(x_i)}{\sigma_i} \right)^2, \tag{4.6}
\]

where \(\sigma_i\) are the known uncertainties in the data.[59]

(a) The mean relaxation times of glycerol as a function of temperature.

(b) Logarithmic mean relaxation times of glycerol as a function of the inverse temperature, rescaled by 1000/\(T\).

Figure 4.17: Mean relaxation times ((\(\langle \tau_K \rangle \approx 1.5\tau_K\)) as a function of temperature for glycerol at the peak of the structure factor, \(q = 14\) nm\(^{-1}\). The Arrhenius fits (red curves) to the blue data points yielded for (a) \(E_a = 63.2\) kJ mol\(^{-1}\) and for (b) \(E_a = 63.5\) kJ mol\(^{-1}\).

Table 4.6: Parameters of the fits in Figure 4.17 using the Arrhenius equation.

<table>
<thead>
<tr>
<th></th>
<th>(T)</th>
<th>1000/(T)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\langle \tau_0 \rangle)</td>
<td>(4.3 \times 10^{-12}) ns</td>
<td>(4.5 \times 10^{-12}) ns</td>
<td>This work</td>
</tr>
<tr>
<td>(E_a)</td>
<td>63.5 kJ mol(^{-1})</td>
<td>63.2 kJ mol(^{-1})</td>
<td>This work [57]</td>
</tr>
</tbody>
</table>
4.3.4 **Vogel-Fulcher-Tammann (VFT) equation**

The Vogel-Fulcher-Tammann (VFT) Equation is

\[
\tau_k[T] = \tau_0 \exp \left[ \frac{D_T T_0}{T - T_0} \right]
\]

where \( \tau_0 \) is the relaxation time at high temperature, \( D_T \) is a fragility strength coefficient which is material-dependent, and \( T_0 \) is the Vogel divergence temperature \((T_0 < T_g \text{ and } T > T_g)\), where \( T_g \) the glass transition temperature.\([60]\) It is a modified version of the Arrhenius Equation (4.4) which can be used to describe the relaxation times of liquids as a function of temperature.\([61]\) It has a strong temperature dependence in the supercooled regime and it is the most popular method for understanding the behavior of glassy materials.

Figure 4.18(a) shows the mean relaxation time as a function of temperature and Figure 4.18(b) shows the logarithmic mean relaxation time as a function of inverse temperature, where the fit to the VFT Equation (4.7) is the red curve through the blue data points. A comparison of the \( \chi^2 \) values from the Arrhenius and VFT fits show that the VFT relationship fits the data better. The gray data points are relaxation times not used in the calculations. The fit parameters used for the VFT fit (red curves) are shown in Table 4.7.

The fragility \( m \) is a metric describing the behavior of the Arrhenius equation via a straight line or curve in the “Angell Plot” and can be used to find the glass transition \( T_g \).\([52]\) The amount of curvature is indicative of the fragility of the glass former. Materials that are considered “strong” glass formers (small \( m < 30 \) values) display more of a linear Arrhenius-type curve upon cooling (the red curve in Figure 4.19). Materials that are considered “fragile” glass formers (large \( m > 30 \) values) display more of a non-linear Arrhenius-type curve.
(a) The mean relaxation time of glycerol as a function of temperature

(b) Logarithm of the mean relaxation time of glycerol as a function of the inverse temperature, rescaled by $1000/T$.

Figure 4.18: Relaxation time as a function of temperature for glycerol at the peak of the structure factor, $q = 14 \text{ nm}^{-1}$. The VFT fits (red curves) to the blue data points.

Table 4.7: The fitting parameters using the VFT Equation for the fits in Figure 4.18.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_0$</td>
<td>$0.04 \pm 0.40 \text{ ns}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$0.03 \pm 0.08 \text{ ns}$</td>
<td>3.94 fs [61]</td>
</tr>
<tr>
<td>$D_T$</td>
<td>$5 \pm 13$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$5.1 \pm 3.5$</td>
<td>15.8 [61]</td>
</tr>
<tr>
<td>$T_0$</td>
<td>$150 \pm 73 \text{ K}$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$151 \pm 21 \text{ K}$</td>
<td>132 K [61]</td>
</tr>
<tr>
<td>$m, T_g$</td>
<td>$51, 190 \text{ K}$</td>
<td>[62]</td>
</tr>
<tr>
<td></td>
<td>$53, 189 \text{ K}$</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>$49, 188 \text{ K}$</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>$53, 185 \text{ K}$</td>
<td>[61]</td>
</tr>
<tr>
<td>$T_g$</td>
<td>$185 \text{ K}$</td>
<td>This work</td>
</tr>
</tbody>
</table>

upon cooling (the purple curve in Figure 4.19). These materials must be fit with the VFT relationship.[35]
Figure 4.19: The fragility plot showing the logarithm of the relaxation times as a function of inverse temperature. Materials that are strong glass formers exhibit an Arrhenius type growth of the relaxation times upon cooling, while fragile glass formers show a much steeper temperature dependence close to the glass transition.

The \( m \) is found from find the slope of the VFT relationship. Letting \( T = \frac{T_g}{x} \) as \( T \to T_g \) gives

\[
m = \frac{d}{dx} \left( \log_{10} \left[ \tau_0 \exp \left( \frac{D_T T_0}{T_g - xT_0} \ln 10 \right) \right] \right) \bigg|_{T \to T_g}.
\]

\[
m = \frac{d}{dx} \left( \log_{10} \left[ \tau_0 \right] + \frac{D_T T_0 x}{(T_g - xT_0) \ln 10} \right) \bigg|_{T \to T_g} = \frac{(T_g - xT_0) \ln 10 \frac{d}{dx} [D_T T_0 x] - (D_T T_0 x) \frac{d}{dx} [(T_g - xT_0) \ln 10]}{[(T_g - xT_0) \ln 10]^2} \bigg|_{T \to T_g}
\]

\[
= \frac{D_T T_0 (T_g - xT_0) + D_T T_0^2 x}{(T_g - xT_0)^2 \ln 10} \bigg|_{T \to T_g} = \frac{D_T T_0 T_g}{(T_g - xT_0)^2 \ln 10} \bigg|_{T \to T_g}
\]
Substituting back in $T_g = x$ gives the fragility factor,

$$
\frac{D_x T_0}{T_g \left(1 - \frac{T_0}{T_g}\right)^2 \ln [10]} \bigg|_{T \to T_g}
$$

$$
m = \frac{D_x T_0}{T_g \left(1 - \frac{T_0}{T_g}\right)^2 \ln [10]}
$$

(4.8)

Using the fit parameters and an average of the $m$ values ($m = 51.5$) from Table 4.7 gives a glass transition temperature for pure glycerol of $T_g = 185$ K. [47, 62, 63]

$$
T_g = \frac{D_x T_0}{m \ln [100]} \left(1 \pm \sqrt{1 + \frac{m \ln [10000]}{D_x}}\right) + T_0
$$

(4.9)

$$
= \frac{(51.5)(151 \text{ K})}{(51.5) \ln [100]} \left(1 + \sqrt{1 + \frac{(51.5) \ln [10000]}{(5.1)}}\right) + (151 \text{ K})
$$

$$
= 185 \text{ K}
$$

From the literature $T_g$ can be between 178 K to 193 K [47, 51, 61–63]. For the pure glycerol sample used in this thesis, the glass transition temperature was estimated to be around 185 K which agrees reasonably well with the literature values.

The VFT equation which is used to describe the relaxation times of a liquid as a function of temperature in the supercooled regime shows the fragility of the liquid sample and can be useful in determining the glass transitions of a sample. This is the main reason of using the VFT equation versus the Arrhenius equation. The Arrhenius equation is useful in determining the activation energy, whereas the VFT equation is better at determining the glass transition.
4.3.5 de Gennes narrowing

De Gennes narrowing is a phenomenon in which the relaxation time of a liquid sample is proportional to the static structure factor, $S(q)$. To accomplish this measurement a new annular slit was needed to be fabricated with a smaller width to reduce the $\Delta q$. This new slit had a width of 0.2 mm, which meant a reduction in count rate to a few counts per second. Table 4.8 shows the relaxation times at various momentum transfers when the glycerol was at $T = 250$ K. The data points for $q = 23.1$ nm$^{-1}$ and $q = 29.5$ nm$^{-1}$ used a larger annular slit width of 1.0 mm. Figure 4.20 shows the momentum transfer dependence as a function of relaxation time. There is no general formula that expresses de Gennes narrowing.

![Figure 4.20: de Gennes narrowing of glycerol using 0.2 mm (blue circles) and 1.0 mm (red square) annular slits at 250 K.](image-url)
During this experiment the glycerol may have been frozen instead of supercooled. Figure 4.21(a) shows the NR-TDI data from a previous experiment using an annular slit width of 1.0 mm and cooling rapidly down to 150 K before starting to make measurements. Figure 4.21(b) shows a run from the de Gennes experiment where the sample was cooled to around 250 K and used an annular slit width of 0.2 mm. A different sample holder, Figure 3.21(c), was used for de Gennes experiment. An indication that the sample was frozen is the shape of the NR-TDI data, as seen in Figure 4.21. The difference between the heights of the peaks, in Figure 4.21 at times around 28, 42, 58, 72, 84, and 101 ns, are very different. The peaks of the supercooled glycerol, Figure 4.21(a), are not showing the zipper pattern seen in Figure 4.21(b). The zipper peak pattern is a telltale sign of a frozen sample or faster relaxation times. However, despite these issues the result from the data is similar to that found in literature.[64]

The knowledge gained from this experiment demonstrates the importance of supercooling the sample before collecting data. A key aspect of understanding the fragility of a liquid sample is understanding the molecular dynamics when supercooled. Being able to visually see if a sample is frozen or supercooled can prevent the loss of experimental time when studying the supercooled regime. The $\Delta q$ resolution using the 0.2 mm for de Gennes narrowing is more than adequate for future de Gennes narrowing experiments.
Table 4.8: Table of de Gennes narrowing data for glycerol using 0.2 mm and 1.0 mm annular slits at 250 K.

<table>
<thead>
<tr>
<th>$q$ (nm$^{-1}$)</th>
<th>$\tau_K$ (ns)</th>
<th>$\langle \tau_K \rangle$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11.4 ± 0.6</td>
<td>177 ± 80</td>
<td>266 ± 121</td>
</tr>
<tr>
<td>12.7 ± 0.7</td>
<td>322 ± 145</td>
<td>485 ± 218</td>
</tr>
<tr>
<td>13.1 ± 0.8</td>
<td>441 ± 244</td>
<td>664 ± 367</td>
</tr>
<tr>
<td>14.4 ± 0.9</td>
<td>370 ± 95</td>
<td>557 ± 144</td>
</tr>
<tr>
<td>15.6 ± 1.0</td>
<td>132 ± 35</td>
<td>199 ± 52</td>
</tr>
<tr>
<td>17.0 ± 1.2</td>
<td>142 ± 33</td>
<td>214 ± 50</td>
</tr>
<tr>
<td>19.8 ± 1.5</td>
<td>99 ± 9</td>
<td>148 ± 13</td>
</tr>
<tr>
<td>23.1 ± 4.0</td>
<td>74 ± 22</td>
<td>111 ± 33</td>
</tr>
<tr>
<td>29.5 ± 6.0</td>
<td>52 ± 17</td>
<td>78 ± 26</td>
</tr>
</tbody>
</table>

Figure 4.21: NR-TDI results for $q = 14$ nm$^{-1}$ and $T = 250$ K showing the difference between being (a) supercooled and (b) frozen.
CHAPTER 5
CONCLUSION

This thesis introduced a new optical component, a gold annular slit, that increases the count rate by two orders of magnitude at the peak of the structure factor in NR-TDI measurements. This component also makes it possible for off peak measurements that previously had low count rates. This technique of using the annular slits is incredibly difficult and we were able to achieve experimental results where others have given up using them because of their difficulties. The experimental setup permits one to easily adjust the momentum transfer by simply changing the distance between the detector and annular slit. This also allows for rudimentary $S(q)$ measurements using the APD detector. The annular slit $\Delta q$ was shown to depend on three major factors: the width of the annular slit, the sample thickness, and distance from the sample. In this thesis I present a clear model representing the experimental setup for NR-TDI using a stationary foil resonant system with a non-resonant liquid sample. Extensive numerical analysis was carried out to determine the contrast and sensitivity of the experiment. For glycerol, temperature dependent measurements were performed over a wide range of momentum transfers ranging from 2 to $30 \text{nm}^{-1}$ and three different annular sizes (0.2, 0.5, and 1.0 mm), improving the understanding of the molecular dynamics of glycerol and increasing the count rate.

The first attempt at this experiment started out with a single APD detector and using two stainless steel foils. One of the foils was attached to an oscillating Mössbauer drive to create a two-line resonance system. With this complex system, data collection was painstakingly slow. The second attempt simplified the experimental setup by replacing the moving stainless-steel foil with a stationary magnetized $\alpha$-$^{57}\text{Fe}$ foil to create a three-line resonance system. This
improvement simplified the experimental setup but did little for improving the count rate. To increase the count rate, our third attempt tried adding two extra APD detectors (for a total of three APD detectors positioned to measure the same momentum transfer) and summing the three detectors’ delay counts together. This setup did improve the count rate but aligning all the detectors at the same momentum transfer and ensuring all three detectors’ electronic timing systems were synchronized was problematic. After much discussion I decided to use an annular slit and manufactured a 1 mm, a 0.5 mm, and a 0.2 mm annular slit. An annular slit allows the entire x-ray diffraction ring, at a particular $q$, to be collected instead of only a fraction of it. With the annular slits the count rate was increased by two orders of magnitude at the structure peak. This new method increased the count rate and enabled the collection of multiple data points at various temperatures and momentum transfers. With the annular slits increasing the amount of data collected, it will naturally give rise to a better understanding of the molecular dynamics of liquids.

The scattering intensity for a two-line $\alpha^{57}$Fe foil (source), a single-line stainless steel foil (analyzer), and a non-resonant sample was modeled on Smirnov’s theory. The scattering intensity relationship assumed radiative coupling was small and was therefore valid in the “quantum beat” regime. The scattering intensity describes the time-dependent interference of nuclear resonant electric fields with a non-resonant liquid sample as a function of momentum transfer and temperature. This interference gives insight into the molecular dynamics of a liquid sample, especially in the supercooled regime. The Kohlraushs–Williams–Watts, Arrhenius, and Vogel–Fulcher–Tammann equations provide models of the molecular dynamics of liquid samples and enables the extraction of relaxation times, non-ergodicity factors, electronic absorptions, and stretching exponents as a function of temperature and momentum transfer.

Due to the large increase in count rate, it is now possible to perform measurements at different momentum transfers that were once considered unrealistic. Measurements were
made using the 0.5 mm and 1.0 mm annular slits at momentum transfers of $q = 2, 5, 7, 10, 14,$ and $20 \text{ nm}^{-1}$ at temperatures ranging from $190 \text{ K}$ to $300 \text{ K}$ by means of this technique. The exploration of de Gennes narrowing was also possible using a 0.2 mm annular slit at momentum transfers of $q = 11.4, 12.7, 13.1, 14.4, 15.6, 17.0, 19.8, 23.1,$ and $29.5 \text{ nm}^{-1}$ at 250 K. These annular slits allow for the collection of almost the entire diffracted ring of x-rays at any momentum transfer between $1 \text{ nm}^{-1}$ to $100 \text{ nm}^{-1}$ and relaxation times between 1 ns to 10,000 ns using a standard single $10 \times 10 \text{ mm}$ APD detector.

The use of annular slits can be the key factor for a better understanding of the molecular dynamics of liquid samples and as a function of temperature, momentum transfer and pressure in the supercooled regime. The Arrhenius and VFT provides the ability to determine the activation energy, fragility, and glass transition temperature of liquid samples. These slits make it possible to collect more data in shorter amounts of time, allowing for more data points at various temperatures, momentum transfers, and pressures. With this extra data, it could be the answer to unlocking some of the unknowns about the supercooled dynamics of liquids.

This thesis successfully implemented the use of an annular slit that improved the count rate by two orders of magnitude, with only a slight increase in $\Delta q$. I successfully modeled a three-line NR-TDI system for a non-resonant liquid sample (having no Mössbauer isotopes), and I was able to obtain relaxation times as a function of temperature and momentum transfer. Using these relaxation times, I determined that the glass transition temperature of glycerol was $T_g = 185 \text{ K}$ and its activation energy was $E_a = 63 \text{ kJ mol}^{-1}$ (when using a fragility value of $m = 51.5$).
5.1 Experimental Improvements

There are several ways to make improvements for future NR-TDI experiments. To increase the $q$ resolution one can increase the size of the APD detector collection area. Then the detector can be placed further from the sample, thereby reducing $\Delta q$. With the current setup the APD detector has a square area of $10 \times 10 \text{mm}$. At $q = 14 \text{nm}^{-1}$ the distance between the sample and detector is $L = 20.6 \text{mm}$ with $\Delta q = \pm 2.7 \text{nm}^{-1}$ for the $1.0 \text{mm}$ annular slit. Suppose the square area of the APD detector is double to $20 \times 20 \text{mm}$ using the same $1.0 \text{mm}$ annular slit. Then the distance between the sample and detector must increase to $L = 41.2 \text{mm}$ resulting in a smaller $\Delta q = \pm 1.3 \text{nm}^{-1}$. This is the major advantage of using a larger area APD detector because the $\Delta q$ improves dramatically. The $\Delta q$ reduces even more for narrower annular slits. For instance, $\Delta q = 0.9 \text{nm}^{-1}$ for $0.5 \text{mm}$ annular slit and $\Delta q = 0.6 \text{nm}^{-1}$ for $0.2 \text{mm}$ annular slit. Another benefit of using a larger area detector is the range of measurable momentum transfers. With the current setup, the minimum distance between the cover on the cryostat and the sample is approximately $10 \text{mm}$. This puts a limit on the maximum momentum transfer of $q = 25 \text{nm}^{-1}$ because the distance between the sample and detector cannot be physically any closer. With the same minimum distance of $10 \text{mm}$, the $4 \text{cm}$ area larger detector can have a maximum momentum transfer of $q = 50 \text{nm}^{-1}$ using a $0.2 \text{mm}$ annular slit. This increases the maximum range of measurable momentum transfers from $q = 25 \text{nm}^{-1}$ to $q = 50 \text{nm}^{-1}$. Therefore, increasing the area of the APD detector not only improves the $q$-resolution, but also increases the upper limit of momentum transfers using the current setup.

Having a designated space with a permanent setup of stages and motors would allow precise and accurate measurement for distances between the sample and annular slit, decreasing the experimental uncertainties in measurements. Knowing the distance between the sample
and annular slit determines the momentum transfers. The current method of using scan at different distances between the sample and annular slit to find the maximum scattering intensity and comparing it to the $I(q)$ scan from the single-photon counting pixel detector the to define the momentum transfer is adequate but needs improvement.

With the annular slits one can use the more complex six-line energy spectrum from an unmagnetized $\alpha$-$^{57}$Fe foil possible. In theory this would increase the count rate, but it was never tested because of its complexity and the uncertainty in how much it would increase count rates are not known.

The APS upgrade will still permit NR-TDI to continue at Argonne National Lab. The upgraded beam will be 500 times brighter. The beam emittance will also be reduced increasing the focusing capability of the beam onto a smaller area, thereby increasing the $q$-resolution for NR-TDI experiments. This will dramatically increase the count rate. The upgrade will double the number of bunches going from 24 bunch mode to 48 bunch mode. Thus, the timing window for NR-TDI measurement will go from 153 ns to 76.7 ns. With the new shorter timing mode there will still be enough time to capture the first couple of contrast peaks needed to calculate the relaxation times of liquid samples. We look forward to the APS upgrade and will continue with NR-TDI experiments in the future.


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