ANALYSIS OF DISLOCATION PIPE DIFFUSION IN
DEFORMED $\alpha$-PHASE PdH$_x$ USING A SYNTHESIZED QENS
APPROACH

BY

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Abstract

Using quasielastic neutron scattering results from multiple spectrometers, material considerations are made for annealed and deformed PdH_x with sufficiently low [H] as to encourage the process of dislocation pipe diffusion (DPD) below a critical temperature. The results of this analysis indicate that the simultaneous comparison of QENS results from instrument with different instrumental resolution and energy transfer window can provide a more comprehensive picture of the diffusive modes seen within a system than using the instruments independently. A method is developed for accurately comparing the dynamic structure factor $S_{inc}(Q,E)$ data of multiple instruments, using an inverse Fourier transform in order to obtain the intermediate scattering function $F_{inc}(Q,t)$ for each instrument and simultaneously analyzing the output from three QENS spectrometers. An array of models are approached to describe the combined $F_{inc}(Q,t)$, with the best description of $F_{inc}(Q,t)$ for the deformed PdH_x found to be a summed KWW/single exponential fit. The results show that the DPD contribution to the $F_{inc}(Q,t)$ can be well described using a stretched exponential (KWW) mode, which is qualitatively correlated to the heterogeneity of the diffusive modes expected for the near-core and inner core region of heavily deformed Pd.
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Chapter 1

Introduction

1.1 Background

First acknowledged in 1866 by chemist Thomas Graham [1], the palladium hydride system quickly became a subject of study for fundamental metal-hydrogen interactions due to the metal’s affinity for rapid absorption of hydrogen. In the 1960s, Pd-H alloys were chosen as a benchmark material for foundational academic investigations into metal-hydrogen interactions using the newly developed technique of neutron scattering [2, 3, 4]. Due to a high rate of hydrogen solubility that can be easily quantified [5, 1, 6, 7], Pd-H interactions can be considered more than just an academic benchmark and may provide solutions to the dilemma of manufacturing hydrogen based grid-scale energy storage. On a macroscopic level, hydrogen interactions with a metal can alter the ductility, strength and fracture toughness of a material [8, 9]. When considering material applications within a hydrogen-rich environment, including situations such as the hydrogen fuel cell, nuclear fuel cladding and similar situations where the possibility for rapid oxidation and hydrogen absorption is high, the understanding of these interactions at both the macroscopic and microscopic level is essential [10].

Two principal goals exist for the scientific insight presented. Firstly, notable improvements to the methods used for analysis of quasielastic neutron scattering data have been made, as a method has been developed for the simultaneous comparison of condition-specific data from instruments of varied energy domains. It is postulated that successful analysis on data from two distinct QENS instruments can be performed by transforming the experimentally obtained dynamic structure factors \( S(\vec{Q}, \omega) \) from dissimilar energy domains into the comparable domain of time, effectively creating a range of output that can be treated as an intermediate scattering function \( F(\vec{Q}, t) \) [11]. Due to differences in ability to distinguish information about the system at different energy resolutions (meV versus \( \mu \)eV scales), comparing data from both instruments in the time domain gives a clearer view into the system dynamics. Additionally, from the results, it is hoped that further insight into the diffusion mechanism described as dislocation pipe diffusion will be ascertained. In systems with a significant amount of dislocations (highly deformed), it has been proposed that the rate of diffusion of
small impurities such as hydrogen can be larger than their assumed levels due to the ability of the hydrogen to use these linear defects as diffusion pathways. QENS has previously been used as a method for directly measuring this change in diffusion mechanism [12]. By applying QENS over a varied energy range on a system that displays a theoretically simple diffusion mechanism in the bulk form, data has been gathered about the rate of diffusion of $\alpha$-phase PdH$_x$ at an array of temperatures for both deformed and annealed palladium. These results can then be compared directly with other experiments performed historically on bulk PdH$_x$ samples to ensure proper calibration of the method used, and subsequently help determine quantitatively how the introduction of dislocations into a PdH$_x$ sample can contribute to the activation energy of diffusion for H atoms.

A detailed review of previous investigations into the PdH$_x$ system with emphasis on using QENS as a tool of analysis will be performed in Chapter 2. Some insight into methods applied for analysis of QENS data from distinct instruments will also be presented, as well as discussion on the physical theory behind dislocation pipe diffusion and previous research on this phenomenon. Explanation of the theoretical basis for diffusion mechanism as well as for how the data will be analyzed is given in Chapter 3 while Chapter 4 will outline the experimental and analytical methods used to gather information about the system and produce meaningful results computationally. This is followed by a discussion on the results obtained, and on the level of success of various methods tested for simultaneous analysis of QENS data.
Chapter 2

Literature Review

2.1 The PdH\textsubscript{x} System

Discovered by William Hyde Wollaston in 1803 while dissolving platinum in nitric and hydrochloric acid, palladium (Pd) began as an ornamental device, useful for jewelry due to its malleable nature \[10\]. More recently, palladium has been proven to have large-scale materials science applications. The passing of the Clean Air Act of 1990 by the U.S. EPA led to an increase in the use of catalytic converters using Pd alloys as an oxidation catalyst in order to efficiently break down common pollutants \[10\]. Industrialized countries are striving to significantly decrease CO\textsubscript{2} emissions in the 21st century, which has encouraged continual efforts to improve the catalytic capability. In addition to this oxidizing attribute, platinum group metals and Pd in particular have another impressive quality, namely their capacity to absorb hydrogen gas and retain large quantities of it in solid solution. While this characteristic of Pd could be extensively useful in modern applications, the cost of procuring Pd and the element’s heaviness are limiting factors in its use as a hydrogen storage medium.

The first mention of this absorptive capability occurs in Thomas Graham’s experiments with a Bunsen cell in 1866, using a variety of metals as substitutes for the standard zinc anode component. He noted that although platinum and iron did intake hydrogen from the system, the “occulsion” (a term used to describe the absorption of a gas into a metal by the entire metal volume) of hydrogen into Pd far exceeded that of other tested materials, with a calculated hydrogen uptake of 200 to 900 times the volume of the Pd sample \[1\]. He documented that hydrogen could not escape at the testing temperature (285 K) but that it would vacate while raising the sample temperature to 373K. After switching the direction of current in the cell, he concluded that the absorption mechanism only could apply to the hydrogen atom, as the introduction of oxygen caused the hydrogen to vacate and was not itself absorbed.

More insight into this mechanism was obtained in two separate studies using Pd as the cathode of an electrolysis reaction. As discovered by Lambert and Gates \[5\], placing Pd in an isothermal H\textsubscript{2} environment at differing equilibrium pressures led to distinct absorption and desorption processes. Interestingly, while the desorption process showed a region of constant equilibrium pressure
within the Pd sample over a range of concentrations (.1 < [H]/[Pd] < .5) as hydrogen vacated the system, the absorption process demonstrated a near-linear increase between the applied H\textsubscript{2} pressure and the quantity absorbed within the sample over the same region. The processes also differed in that the desorption mode was replicable over a range of temperatures, while the absorption yielded distinct changes in necessary H\textsubscript{2} pressure per each performed test. Additionally, a maximum solubility of [H]/[Pd]=.6 is established. Building off these investigations, Ubbelohde theorized that although H\textsubscript{2} can be fully absorbed into Pd, the diatomic hydrogen molecule must dissociate into atomic hydrogen before adsorption and is reliant on a surface catalyst to assist the adsorption process \[7\]. Ubbelohde pointed out that the inflection points seen in the desorption process could have designated either a change of phase or a difference between amorphous and crystalline Pd, and that the differences between the absorption processes indicated the existence of a hysteresis mechanism. In this work, it was discussed that Sievert’s law for absorbed hydrogen holds true at low concentrations, namely that the absorbed hydrogen is proportional to \[\sqrt{P_{\text{H}_{\text{external}}}}\]. Ubbelohde also remarked that the heat created through the adsorption process must reflect a chemical change, in which hydrogen is converted from a gas into a proton/electron pair, leading to a characteristic heat of formation for a metal hydride. As a supplement to this theoretical work, Ubbelohde performed his own set of electrolysis experiments, and saw that as the maximum [H\text{external}] increased, the region of constant equilibrium pressure P\text{H} vs. [H]/[Pd] was extended \[6\]. It was then postulated that if the rate of removal at the surface is slow compared to the rate of diffusion, P\text{H} will seem to act essentially constant until the concentration is sufficiently lowered. Ubbelohde saw that activation energy for occlusion is lowered by repeatedly oxidizing and reducing the Pd but restored if the sample is annealed, an effect that was acknowledged to be a direct result of maintained lattice expansion due to metal hydride formation \[6\]. Finally, it is noted that the introduction of excess oxygen appears to poison the adsorption surface, which is likely due to the formation of surface contaminants when foreign components enter the system.

Expanding upon the notion that increased lattice strain contributes directly to the absorption process, Owen performed a set of x-ray analyses on Pd containing different [H], investigating the effects of lattice expansion at the different phases postulated by Lambert and Gates \[13\]. While testing at 373K, Owen’s x-ray results clearly indicated that an \(\alpha\) phase exists with a lattice parameter of around 3.88 Å at low concentrations, while there is solely a \(\beta\) phase at high concentrations, with a lattice parameter near 4.02 Å. This result implied close correlation of the low concentration phase to a previous x-ray study performed on pure Pd \[14\], and verified previous results that showed an FCC crystal structure in Pd \[15\]. At intermediate concentrations, the phase were seen to coexist, and within this coexistence region there was a time dependent relationship between a maintained equilibrium pressure and the increase of strength in the \(\alpha\)
phase line intensity versus that of the $\beta$ phase. Owen also saw a clear correlation to $[H]/[Pd]=.5$, possibly pointing towards the formation of PdH$_2$. Intriguingly, Owen also remarked that the deformation introduced by applying $\beta$ phase $[H]$ led to a lattice that remained permanently deformed unless ample temperature was applied to relax the strain. In an effort to create theoretical bounds for the phases seen, Tanaka and Harasima performed a modification to the theory of Lacher, who originally used statistical thermodynamics to postulate a partition function and likewise calculate the Helmholtz free energy and chemical potential for the PdH system. Lacher proposed a concentration of $[H]/[Pd]=0.27$ at the critical temperature, and also explained the hysteresis loops seen by describing a process in which $\beta$ phase “droplets” create a surface of interaction with the $\alpha$ phase that is not replicated when degassing the PdH, and in fact changes sign in its radius of curvature, leading to variation between the absorption and desorption isotherms. Tanaka, on the other hand, improved upon the proposed symmetric isotherms provided within Lacher’s theory by taking into account nearly full ionization of hydrogen as well as interactions between neighboring protons. These studies relate sufficiently the low concentration transition that occurs within palladium hydrides, as can be seen in Figure 2.1.

As postulated in the discussed sources and as seen in Figure 2.2, a dilute $\alpha$ phase with H in solid solution exists at very low concentrations, determined to be less than $[H]/[Pd]=0.017$, while a high concentration disordered hydride phase exists independently once $[H]/[Pd]=0.63$. The disordered phase has been referred to by various sources as either $\beta$ or $\alpha'$, but shall be referred to strictly as $\alpha'$ here, as this is more properly representative of the phase’s composition. The mixed phase will coexist with these concentrations below a critical temperature of 568 K. Additional work has been performed experimentally that establishes a more ordered set of phases must exist at cryogenic temperatures and concentrations of hydrogen above the $\alpha'$ phase saturation limit, albeit on samples infused with deuterium in some of the tests. However, in this temperature range, it is expected that both isotopes will demonstrate similarly ordered behavior. Below about 53 K, a high concentration ordered phase appears to exist between concentrations $0.61 < [H]/[Pd] < 0.7$ and transitions into a nearly stoichiometric phase denoted with $\gamma$ beyond this concentration, as suggested by early Monte Carlo simulations. However, a recent experimental study using specific heat measurements did not see the existence of these distinct ordered phases, and instead saw a linearly increasing transition in temperature from 55K to 85K between concentrations of $0.6572 < [H]/[Pd] < 0.8753$, contradicting the fully ordered concept. Both of these attempts at describing the appearance of PdH$_x$ at higher concentrations can be seen in Figure 2.2.

The existence of the hysteresis effect first noted by Lambert and Gates and witnessed by future researchers when describing deformations within PdH system is due to a set of contributions. As first postulated through Lacher’s theory, there exist long-range attractive H-H interactions that perpetuate as $[H]$ is
Figure 2.1: Theoretical isothermal curves for the p-x-T relationship between Pd and H, laying the groundwork for the PdH$_x$ phase diagram [10].

decreased when the [H] is initially increased beyond a certain level. Due to the discovery of the Gorsky effect [26], it was determined that an external strain field causing a gradient in the dilatation tensor of a crystal lattice would lead to an [H] gradient following the introduced lattice deformation [27]. Alefeld [28] recognized that the Gorsky effect is directly related to elastic dipole interactions, and that hydrogen contained within FCC metals acts as a lattice gas that undergoes these attractive dipole-dipole interactions at a range longer than the expected metal lattice constant. Alefeld also reasoned that the overall elastic interaction leads to a concentration dependent effect on the heat of solution for hydrogen, which was confirmed by further development of this long-range interaction by
Horner and Wagner [29]. Through the application of mean-field theory for the average elastic contributions of hydrogen interactions, it was shown that these interactions are likely responsible for the “gas-liquid” phase transition (from $\alpha$ to $\alpha'$) when a harmonic metal lattice is assumed to host the hydrogen. Long range H-H interactions in Pd lead to the partial enthalpy and thus the chemical potential to have concentration dependence, which in turn leads directly to the coexistence of phases as postulated originally. The $\alpha - \alpha'$ coexistence region can be said to have undergone a spinodal decomposition, i.e. the creation of two phases without a thermodynamic barrier that is fully dictated by diffusion, and generally is considered to form incoherent (distinct) states. Flanagan and Oates [30] evaluated isotherms against Monte Carlo simulations, and determined that the spinodal decomposition is valid for temperatures close to the critical temperature, and the existence of some slight coherent states leads to the sloped region of the isotherms, such as those in Figure 2.1. With respect to the $\beta$ phase, Alefeld [28] noted that although the secondary effect (the Snoek effect) contributing to the formation of an ordered $\beta$ phase won’t typically exist in an FCC lattice, it is possible at high [H] for the induced strain fields to cause a deviation in dipole moments for pairs of H atoms and individual H atoms, leading to the question of how H-H interacts at a short range. Indeed, as the concentration is significantly increased, various hypotheses have been given as the nature of these interactions, including the existence of repulsive many-body interactions that are not a direct sum of pairwise interactions [31]. Another hypothesis that was previously considered was the band filling of Pd, which was also given as the limiting factor concerning the absorption of further hydrogen atoms. This theory also led to a proposition of the substoichiometric nature of the $\beta$ phase, deducing that the saturation of the 4d electron band and the

Figure 2.2: Pd-H Phase Diagram, displaying the coexistence of the diffuse $\alpha$ phase and the ordered $\alpha'$ phase. $\alpha'$ is referred to in some literature as the $\beta$ phase. Compiled from [19, 20, 21, 22]
subsequent difficulty of overcoming the electronic heat capacity related to filling the 5s band would lead to this relationship. However, this explanation for the nonstoichiometric ordered phase was later replaced by the assumption of hybridization of the H 1s band and the Pd 4d band, leading to an elastic interaction that restricts site occupation \cite{32}. Picton et al. \cite{33} demonstrated how long range attractive H-H interactions can be balanced by short range repulsive interactions at high [H]/[Pd] by evaluating the difference in interaction parameters in the Pd-D system, following the previous models to conclude a possible set of ordered phases below the "anomalous" 50K boundary at high [H]/[Pd].

2.2 Neutron Scattering and The Chudley-Elliot Model

In order to understand the development of modern PdH\textsubscript{x} research, it is crucial to discuss the foundations of the method of neutron scattering, as the improvements made to this technique since its inception have come in tandem with refinement of PdH\textsubscript{x} results. The technique of neutron scattering, specifically of thermal neutrons, arose naturally as a research tool in the late 1950’s due to the abundance of neutrons that could be harnessed from newly developed nuclear reactor technology. In addition to a high flux, the neutron has significant advantages over previously used scattering techniques for many applications. Thermal neutrons harnessed from a reactor have a de Broglie wavelength that is comparable to lattice parameters in a variety of substances, and also have energy that is of similar magnitude as a range of excitation types within solids and liquids. This implies that neutrons can be utilized to gather structural information related to the scattering angle as well as the energetics within the scattering system. Neutrons have a magnetic spin, allowing them to provide time-dependent data on the distribution of unpaired electrons within magnetic systems \cite{34}. Additionally, neutrons are preferable over other methods of scattering for specific systems due to their lack of atomic charge. The scattering is solely dependent on the thermal neutron cross section as there is no Coulomb barrier for neutrons to overcome. This leads to the unique capability of this method to discern valuable information about hydrogen in metals. Atomic hydrogen has the highest incoherent neutron cross section amongst all elements (80.27 b), while most metals have such a low scattering interaction with neutrons, such as that of Palladium (.093 b) \cite{35}, that they are approximately transparent to neutron scattering relative to H. Unlike coherent scattering, an incoherent scattering process describes the dynamics of individual particles and not the collective nuclei dynamics, making incoherent scattering a useful tool for probing hydrogen diffusion within a metal. The advantages of the neutron scattering method have led to significant improvements of the technique beyond the initial reactor based applications, specifically with the innovation of high
precision neutron sources such as the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. While both reactor and spallation applications have the capability to tune the incident energy of the neutron beam using a system of choppers, employing the time-of-flight detection method for determining the neutron energy loss is made significantly more efficient by using a spallation source. Detailed information about a scattering system can be gathered by analyzing both elastic and inelastic scattering of neutrons in a system. In order to distinguish the two methods, it is important to distinguish changes in momentum from changes in energy of the neutrons upon scattering. Upon elastic scattering, the incident energy of the incoming neutron will remain consistent as it is scattered, while some of the momentum of the neutron will be transferred as it is scattered. This implies that although \( E_i = E_f \) in elastic scattering, the momentum of the neutron will change such that \( \mathbf{k}_i - \mathbf{k}_f = \mathbf{Q} \), where \( \mathbf{Q} \) is the vector quantity of the momentum transfer. In the inelastic scattering case, \( E_i - E_f = \hbar \omega = \Delta E \neq 0 \), while the value of \( \mathbf{Q} \) is frequently still variable. This allows for a full range of information that can be acquired about the scattering system, as is evident in Figure 2.3. The information yielded corresponds directly to the dynamic structure factor for the scattering system, and is represented by \( S(\mathbf{Q}, \omega) \). As will be further discussed in Chapter 3, the dynamic structure factor is a direct result of the double differential neutron cross section, and can likewise be segmented into coherent \( S_{\text{coh}}(\mathbf{Q}, \omega) \) and incoherent \( S_{\text{inc}}(\mathbf{Q}, \omega) \) terms respectively. The range of accessible \( \mathbf{Q} \) and \( \Delta E \) is primarily dependent on the configuration of the neutron scattering instrument at hand and the available incident neutron energy.

Figure 2.3: Range of dynamical modes that can be determined via inelastic neutron scattering, as a function of energy transfer.

As can be seen, a wide array of excitations can be probed, including rotational and vibrational modes, recoil of small scattering elements, and electronic transitions. One of the most interesting features of this range can be seen at small incident neutron energies, at a few meV and lower. Known as quasielastic neutron scattering (QENS), this intermediate scattering mechanism constitutes of a peak broadening with respect to the \( \Delta E \) axis that manifests itself as an increase in the full width at half maximum (FWHM) while remaining centered.
very near to the elastic peak. Modern experiments invoking the QENS method can use sufficiently low incident neutron energies in order to eliminate contributions from inelastic scattering modes. However, inherent to QENS analysis is the expectation that the spectrometer used will have an imperfect energy transfer regime near the elastic region, which leads to an additional broadening in the overall $S_{\text{inc}}(\tilde{Q}, \omega)$ output. Chapter 3 will provide further insight towards the theoretical development of QENS output analysis, and how the additional contributions are accommodated. The experimental applicability of this method will be further expanded upon in Chapter 4, and insight will be given into how the applied instrument’s tuning parameters affect the range of useful data provided. For the purpose of the current discussion, it will suffice to point out that the $\tilde{Q}$ range for typical inelastic spectrometers (including backscattering spectrometers) is $0.2 \, \text{Å} < \tilde{Q} < 2.0 \, \text{Å}$, with possible instrumental resolutions on the order between $10^{-1} - 10^{2} \mu\text{eV}$. Since the theoretical basis of QENS analysis will be presented in full later, it is important to note here the historical progression of how the early development of these models were improved alongside improvements in precision of experimental data for the PdH$_x$ system. The small amount of energy transfer inherent to the QENS broadening was initially attributed to Fickian diffusion [11], assuming that diffusing particles undergo Brownian motion. Around the time that the first neutron scattering experiments were being developed, derivations of the expected structure factor for the experiments were discussed for simple systems. It was determined that while Fickian diffusion yielded a quantitative dependence of the broadening of the QENS peak directly proportional to $DQ^2$, this simple model did not hold when larger Q values were analyzed, and in fact a significant damping effect was seen after a certain Q was reached. Since larger Q values are equivalent to smaller magnitudes in real space, as Q is the magnitude of a vector in reciprocal space that is a direct Fourier transform of real space, this dampening must be the result of interactions within the scattering system on the order of the system’s structural parameters. It was postulated by Chudley and Elliot in 1960 that in this case the discrete nature of the diffusive process is no longer a negligible factor, differing from the assumption of Brownian motion made within the Fick’s law derivation. Instead, the length has a nominal value relative to the motions of the particle. As a result, two characteristic times must exist within a “structured” liquid, namely a residence time during which the particle is not diffusing but rather thermally oscillating and a jump time over which the diffusion actually occurs [3]. By assuming this jump time to be negligible compared to the residence time of a particle, it was determined that a particle undergoing “jump diffusion” should see a dampening in the QENS broadening as Q increases beyond a certain value that is inversely proportional to the residence time. As will be revealed mathematically in Chapter 3, the peak broadening due to QENS seen by a single jump diffusion process is postulated to resemble a single Lorentzian function,
\[ S_{inc}(\omega) \sim L(\omega) = \frac{2\Delta \omega}{\Delta \omega^2 + \omega^2} \] (2.1)

which can be clearly distinguished once the effects of elastic scattering and instrumental resolution are deconvoluted from the output. This theory was shortly thereafter adopted for the analysis of low concentrations of hydrogen in the Pd lattice by Sköld and Nelin \[37\], as the model could yield information not only about the discrete jump length and residence time of the jump diffusion mechanism, but also directly provided (via Einstein’s relation for diffusion) the diffusion constant \( D \) for the hydrogen contained within the given scattering system. This capability proved very inviting to experimenters who wished to determine directly 1) where the hydrogen positions itself within the FCC Pd lattice and 2) how quickly hydrogen contained with the lattice could diffuse throughout the Pd, without significant interference from the Pd lattice itself and while using the latest neutron scattering technology.

### 2.3 \( \text{PdH}_x \) Research near the Dawn of Neutron Scattering Experiments

Before neutron scattering measurements were used to probe the space of \( \text{PdH}_x \) compositions, it had already been verified that Pd contains a basic FCC crystal structure with a lattice parameter of around 3.859 \( \text{Å} \) \[14\]. This agrees well with the results of recent computational studies, which indicate a parameter of 3.885 \( \text{Å} \) at room temperature \[38\]. The previously discussed results of Owen \[13\] demonstrated that there existed a difference in the lattice parameter for the ordered and disordered phases, but no clear indication of where the hydrogen rested within the lattice was given. On the other hand, McKeehan \[15\] indicated that hydrogen most likely would be found at the tetrahedral interstitial sites within the FCC Pd lattice via an x-ray investigation. Once neutron scattering capability was realized in the late 1950’s, Worsham et al. \[2\] decided to further investigate these assertions using neutron diffraction. This study documented results for three concentrations, namely a strictly \( \alpha \) and \( \alpha' \) concentration (\( \text{PdH}_{0.07} \) and \( \text{PdH}_{0.706} \)) set during H absorption and an additional \( \alpha \) concentration (\( \text{PdH}_{0.064} \)) after removal. A rocksalt structure was predicted, as shown in Figure 2.4, and for the high concentration phase this hypothesis was seemingly validated by the diffraction planes, in that the intensities of the diffraction peaks showed that H could be found within the same planes as Pd. Worsham et al. did not see conclusive results for \( \alpha \) phase structure, but indicated that the \( \alpha' \) still exists in the \( \alpha \) phase diffraction pattern, which is logical due to the use of a concentration slightly above that of diffuse phase boundary. In this study, a suggestion for the motion of hydrogen in bulk Pd is made. Due to a scattering cross section similar to that of free hydrogen, it is suggested that “jump diffusion” could be occurring as a result of thermal motions in H and a relatively
weak Pd-H bond, allowing H to hop between empty sites in the lattice. Bergsma and Goedkoop [4] verified this rocksalt structure using a diffraction setup, and also used an inelastic neutron scattering setup on PdH$_{0.63}$ to determine two harmonic vibrational peaks at about $\hbar\omega = 56$ meV and 120 meV. It is also noted that the Debye temperature for this high concentration sample was close to 300K, higher than that of pure Pd (275K).

![FCC structure of Pd, with available octahedral sites for H demarcated](image)

**Figure 2.4:** FCC structure of Pd, with available octahedral sites for H demarcated [2].

### 2.4 QENS Based Diffusion Research in Bulk/Single Crystal PdH

While the Chudley-Elliot method was developed with the intention of analyzing a liquid close to the melting point [3], the model was quickly able to be applied to QENS results for the PdH$_x$ scattering system. Although relatively simple, the isotropically averaged jump diffusion model was seen to be the only valid model that correctly documented the oscillations seen by Sköld and Nelin in their 1966 QENS experiment [37]. In this study, a number of important points are developed. At a set of temperatures well above room temperature (582K, 630K, 704K), Sköld and Nelin performed QENS on a Pd plate that was assumed to act as in an isotropic polycrystalline manner. From this study, previous hypotheses about H position within $\alpha$–PdH$_x$ were validated, as the data was described well via the characteristic jump length for distance between Pd octahedral interstitials of 2.75 Å (equivalent to $\sqrt{2}/2 \times a$) [37]. From the Chudley-Elliot model fits to the data, a set of residence times was obtained and subsequently a diffusion coefficient D for each temperature could be found. Using an Arrhenius relationship to model how diffusivity affected temperature,
\[
D = D_0 \exp \left( \frac{E_a}{kT} \right)
\]  

(2.2)

where \( k \) is Boltzmann’s number, an activation energy \( E_a \) of \( 3700 \pm 500 \text{ cal g}^{-1} \text{atom} \) (equivalent to approximately \( 0.16 \text{ eV atom}^{-1} \)) was determined. This value differed significantly from values found using alternate techniques, such as the rapid \( \text{H}_2 \) technique applied just a year earlier that yielded an \( E_a \) of \( 5990 \text{ cal g}^{-1} \text{atom} \) (approx. \( 0.26 \text{ eV atom}^{-1} \)) \cite{39}. Also, a value for absolute diffusion coefficient \( D_0 \) was not explicitly given. A expansion of these preliminary results was published shortly thereafter by Sköld and Nelin, seeking to better establish a theoretical basis for the results \cite{40}. The Chudley-Elliot model was discussed for tetrahedral and octahedral interstitials in the FCC lattice, as well as the need to correct the QENS peak spectra for background and detector efficiency. It was assumed that there would be no “local mode” interference, but the existence of a high energy tail in the QENS data was indicative of a small inelastic effect on the results. It was noted that the scattering results yielded a deviation from the Lorentzian line shape previously postulated at larger values of \( Q \) due to sensitivity of the width to the orientation of \( \vec{Q} \) within the lattice. As a result, a sum of Lorentzians is said to be necessary in order to fully capture the orientational effects within the sample. Although it was determined that the octahedral model correlated best with the gathered data, the isotropic model for Einstein’s relation was applied in order to find the diffusivity. Sköld and Nelin concluded that the change in lattice parameter seen in the \( \alpha' \) phase could be due to \( \text{H} \) ordering as previously described, leading to an anisotropy in jump probability that could be manipulated by performing QENS on a single crystal Pd sample. Following this line of thinking, Rowe et al. proceeded to investigate single crystal PdH\(_{0.3}\) at 623K, and were easily able to verify that jumps between octahedral sites do indeed occur \cite{41}, as seen explicitly in Figure 2.5.

Deviation from the expected Chudley-Elliot model were again seen at value of \( Q > 1.0 \text{ Å} \) in the results of Rowe et al., with the deviation attributed to possible secondary jumps and the existence of a non-negligible jump times between sites. Carlile and Ross, who also investigated single crystal Pd, found that the Chudley-Elliot model was valid for a different set of crystal orientations than those tested by Rowe \cite{42}. Further probing of the PdH\(_x\) system at a range of intermediate concentrations by Sköld and Nelin displayed that the Chudley-Elliot model described the QENS data as correctly as the Gissler/Stump finite jump time model could for a polycrystalline sample, implying that the simpler Chudley-Elliot model was likely sufficient. This investigation concluded that both coexisting phases much have similar diffusive pathways, and pointed out that the lowest \( Q \) value measured was resolution dominated, causing significant uncertainty in the measurement. Kley and Drexel took a different approach to understanding the diffusion process, motivated by differing effects of \( \text{H} \) isotope on diffusion within a single crystal Pd sample, due to the possibility of
Figure 2.5: Comparison of the measured FWHM of the QENS peak as a function of momentum transfer $Q$ for two incident directions (along the [100] and [110] axes respectively) upon a single crystal $PdH_{0.3}$ sample. A fit to the expected Chudley-Elliot jump model is displayed, showing that the octahedral model is the most appropriate choice [41].

Anharmonic coupling of a local vibrational mode from the Pd lattice sites [45]. This study points out that while the localized hydrogen vibrational mode in $\alpha - PdH_x$ will decay via a three phonon process, the $\alpha - PdD_x$ and $\alpha - PdT_x$ processes will decay via only two phonons. Similar to earlier single crystal results, the QENS broadening could not be perfectly described with a Lorentzian or Gaussian function, and it was discussed that the range of FWHM values obtained wasn’t a good fit to the tetrahedral or octahedral jump models used earlier [40]. Regardless of the slight disagreement from the Chudley-Elliot model within polycrystalline (bulk) samples, it was determined by Völk and Alefeld [20] that $\alpha - PdH_x$ has a strongly correlated Arrhenius relationship across a large temperature range, namely between 230K and 800K. By extensively compiling 24 previously performed measurements including many QENS results, as seen in Figure 2.6, Völk and Alefeld established that the expected absolute diffusion coefficient and activation energy for the bulk PdH$_x$ system are $D_0 = 2.9\times10^{-3}$ cm$^2$/s and $E_a = 0.230$ eV/atom respectively. These values have been documented as the most accurate representation of the jump diffusion process at the temperatures in this range in recent texts on metal-hydrogen interactions [19]. Although QENS analysis on bulk/single crystal Pd samples fully established the jump length of the diffusion process as the O-O distance, more recent work has proposed a more likely scenario for the diffusion pathway of hydrogen in crystalline Pd, expecting the hydrogen to follow an octahedral-tetrahedral-octahedral (O-T-O) path due to the lower energy necessary to achieve this type of jump. This pathway takes advantage of the tetrahedral site saddle point, while retaining the expected O-O jump length inherent to the Chudley-Elliot model because this length is path independent. Flanagan and Oates presented a review of the early classical molecular dynamics work [32] and showed how
this type of jump will contain a nominal residence time at the tetrahedral site, which could effectively skew the QENS data at higher Q values. Additionally, low temperature diffusive motion, as shown by the use of the Gorsky effect \cite{19}, will retain a lower activation energy than is expected for the bulk annealed/single crystal process. This behavior can be attributed to a number of effects, including the possibility of quantum tunneling due to multiple phonon interaction between Pd and H. Due to the nature of molecular dynamics, it is not possible to factor quantum mechanics effects directly into the simulation, but through the use of first principles (\textit{ab initio}) simulations it is possible to see these effects. \textit{Ab initio} simulations relevant to the current work will be discussed in more detail in the next section.

Figure 2.6: Detailed compilation of QENS diffusion results, created by Völk and Alefeld in 1978 using results gathered from both bulk and single crystal analyses. Data is presented on axes of log(D) vs. $10^3/T$, which is a typical way to transform data undergoing an Arrhenius relationship into a linear format \cite{20}.

2.5 Deformed PdH Research

2.5.1 Microstructural Considerations of Deformation

As has already been indicated, there exists disagreement between the expected QENS broadening postulated by the isotropic jump diffusion model and what is seen experimentally. This disparity can be attributed to a variety of factors, but they can be summarized by noting that deformed polycrystalline Pd sample
does not maintain the orientational simplicity of the single crystal or annealed polycrystalline tests otherwise performed. As is suggested by the fundamental research in the Pd hysteresis mechanism, there is inherent deformation that is retained in Pd after performing a “cycling” process of increasing, holding and then decreasing [H] within the lattice. The manner is which this deformation manifests itself has been a topic of debate since the hysteresis effect was first measured, with further developments being made as analysis techniques and computational capabilities have improved. Flanagan and Oates [30] gave a qualitative description of the defects introduced by cycling [H] in metals, describing the resulting deformation as a dense network of dislocations which will increase in density as multiple cycling processes are performed. However, it was pointed out that experimental results did not see further plastic deformation beyond the first cycle in a PdH_x sample, which was attributed to dislocations annihilation upon degassing of the sample until a density limit is reached. In its simplest form, a single dislocation can be characterized as a displacement of certain atomic planes within a lattice by a known magnitude, namely Burger’s vector \( \vec{b} \). A classical edge dislocation is described as a one dimensional defect with linear orientation perpendicular to the Burger’s vector, \( \vec{b} \perp \vec{l} \) [44]. For an FCC lattice, which is close packed in the \( \{111\} \) plane, the primitive lattice vectors indicate a Burger’s vector of \( \vec{b} = \frac{a}{2} \langle 110 \rangle \), implying that FCC dislocations will be oriented in the \( \frac{a}{2} \langle 10\bar{1} \rangle \) direction and will engage in slip along the close packed plane. The result of this displacement is a change in elasticity at the base of the displaced planes, the exact character of which has been discussed since the early 1900’s. In the initial construction of Volterra, it was postulated that the displacement occurred continuously using an approximation of a cylinder cut to represent the various dislocation types. However, Burger’s construction of a dislocation in a real crystal indicated that crystal planes would actually undergo a shift in discrete steps equivalent to the separation between them. In the case of a real crystal, elastic relaxation of the system leads to the appearance of the discontinuity in the lattice structure seen in Figure 2.7. Described as the dislocation core, this space is also envisioned as an expanded region immediately below an inserted half plane of atoms that is displaced \( \vec{b}/2 \) from the expected crystal structure.

Peierls and Nabarro [46, 47] expanded upon Volterra’s theory in order to accommodate this discrete atomic construction and the continuity of the dislocation core, and introduced the model further discussed in Chapter 3 that removes the artificial nature of a divergent energy function as the core is approached. The Peierls-Nabarro formulation also provided insight into the creation of partial dislocations, in which additional configurations for the introduced misfit (core) energy for a stable dislocation can lead to the creation of more energetically favorable dislocation structures. In an FCC lattice, this process most often occurs in the form \( \frac{a}{2} \langle 10\bar{1} \rangle \rightarrow \frac{a}{6} \langle 2\bar{1}\bar{1} \rangle + \frac{a}{6} \langle 11\bar{2} \rangle \). When this dissociation of dislocations occurs, the resulting disruption to the lattice can be described as a stacking...
Figure 2.7: Edge dislocation core, as is typical of FCC lattice materials under applied stress. In this simplified model, the dislocation core structure exists immediately below the termination of the inserted half plane of atoms [45]. The aforementioned core structure became a central topic of conversation as researchers began to probe the diffusive nature of interstitials within a deformed lattice, culminating in the introduction of a new theory by Love in 1964. Unlike previous considerations of enhanced diffusivity at low temperatures, Love disregarded the effects that a near-core strained lattice region would have and instead focused on developing the concept of dislocation pipe diffusion (DPD) [48]. Taking into account the need for two diffusivity paths within the core, Love defined the dislocation core structure as the space containing both the elastically broadened region below the inserted half-plane of atoms as seen in Figure 2.7 as well as the line of atoms immediately above this region. In his explanation, Love discussed the probability of a net flux of atoms corresponding to annihilating vacancy-interstitial pairs. In the sense of the dislocation core, Love’s theory implied that this flux would not occur like a lattice Frenkel pair, but would instead appear as the exchange of an interstitial atom below the base line of atoms with a vacant space within this line of atoms. Love predicted that after undergoing dissociation due to the introduction of an interstitial-vacancy pair into the dislocation core, the diffusivity of an atom would show an $E_a$ approximately 1/2 of the expected activation energy for the bulk lattice along with a significant reduction in $D_0$ due to the necessary cooperative atomic motion and expected negative activation entropy associated with this mechanism. Although Love asserted the uniaxial nature of DPD in an edge dislocation, he did not sufficiently describe the physical structure of the core. As a result, no quantitative estimate of the length of a diffusive jump within the core was pro-
vided, and the model was significantly simplified by choosing to use the lattice parameter. Additionally, this base model was developed under the assumption of a pure element, and did not take into account the variability that would occur via the introduction of interstitial H atoms into a lattice.

2.5.2 Hydrogen Trapping and Anharmonicity of Potentials

In the development of the Chudley-Elliot model, no consideration was provided for the introduction of defects into the Bravais lattice structure, indicating that applying this model alone would be only a very rough estimate of the diffusion mechanism. Specifically, as was realized by Love [48], the inherent difficulty of theoretically establishing the expected jump distance within the dislocation would lead to a significant departure from the expected jump length utilized in the CE calculation. In order to gain an understanding of what results may be obtained when doing a QENS analysis on deformed PdH, research performed on the PdH\textsubscript{x} system since Love’s postulation of DPD must be considered. Two main paths of research exist regarding the effects of “cycled” PdH\textsubscript{x} lattice deformation, namely upon investigation and development regarding the true nature of PdH phase formation, as well as explanation of differences in the anharmonicity of energy potentials for H contained within annealed and deformed Pd lattices. In their mean-field derivation of the interactions between H atoms in a lattice, Horner and Wagner [29] had originally assumed a harmonic interaction potential between the atoms, an assumption which will inevitably be violated through the introduction of dislocations assuming that they introduce elastic incongruities. In order to understand how elastic disturbances affect the Pd lattice structure and lead to anharmonicity in the expected energy states for H in Pd, the concept of the Cottrell atmosphere must be introduced. First postulated in 1948 [49], the Cottrell atmosphere mechanism was founded upon the elastic interaction between the induced strain field around loose H in the system and the hydrostatic stress field surrounding dislocations found in deformed Pd. The mechanism dictated that H atoms at lattice interstitial sites will diffuse into dislocation core gaps and relax the hydrostatic stress, pinning the dislocations in place and causing a higher systematic yield stress. Theoretically, this will simultaneously lead to the trapping of interstitial atoms at these pinned sites, since it is potentially the lowest available energy configuration. The concentration of the H within an immediate region around a “filled” dislocation can then be described using a temperature dependent Fermi-Dirac distribution,

$$\frac{C(r, \theta)}{1 - C(r, \theta)} = \frac{C_0}{1 - C_0} \exp\left(-\frac{\sigma_h v}{k_B T}\right),$$  \hspace{1cm} (2.3)

where \(\sigma_h\) is isotropic hydrostatic stress, \(v\) is the volume expansion of hydrogen internally, \(k_B\) is Boltzmann’s constant, \(C(r, \theta)\) and \(C_0\) give [H] within
the dislocation field and isolated from the dislocation respectively, and \( T \) is temperature (in Kelvin) \([50]\). This function accounts for the strong attraction behavior expected of sites below the core as well as the restricted number of core sites. It has been shown that hydrogen in the diffuse \( \alpha \) phase can be preferentially trapped within dislocations in the Pd lattice, a feasible mechanism due to the high dislocation density \((10^{11} - 10^{12} \text{ dislocations/cm}^2)\) created through the cycling process as shown by Jamieson et al. \([51]\). Jamieson et al. also discovered that dislocation formation processes are still engaged during the hydride composition process. Rodrigues and Kirchheim recognized that high local concentration could lead to dominant effects due to the H-H interaction or possible hydride formation in amorphous Pd. Through concentration dependent electrical resistivity measurements, they showed at 298K (close to the expected Debye temperature for \( \text{PdH}_x \) as earlier mentioned) that the hydrogen would become trapped up to about \([H]=10^3 \text{ at. ppm, whereas at higher concentrations the remaining hydrogen was seen to have similar resistivity to samples annealed at high temperature and assumed to be crystalline. Further insight into the investigations of Kirchheim on the effects of hydrogen trapping on diffusivity will be provided in the following section.

In order to probe further into the mechanisms behind the hydrogen-dislocation interaction, an array of small angle neutron scattering (SANS) experiments were performed by Heuser et al. and others in the 1990’s and 2000’s. SANS experiments, which are similar to other neutron scattering investigations but generally at \( Q<0.2 \, \text{Å} \), are attractive for modeling the structure of hydrogen within a metal since interstitial deuterium (as a hydrogen surrogate) with certain orientation will yield a coherent scattering cross section that correlates with the orientation type. Early results by Heuser et al. \([52]\) using deuterium indicated that cycled Pd polycrystalline samples exhibited a \( Q^{-1} \) dependence in their cross section, which was determined to apply only to interstitials oriented in a thin rod, i.e. deuterium trapped within a dislocation core. It is assumed that solute interactions with edge dislocations are the conclusive source of the SANS signal, since perfect screw dislocations will apply no hydrostatic stress effect upon a solute \([53]\). Further investigation of the \( Q^{-1} \) behavior was shown shortly after by Heuser et al. \([54]\), again employing the deuterium scattering cross section to determine that trapped deuterium would remain within a few Burger’s vectors of a trapping dislocation while sitting in a rod-like structure of length on the order of 50-100 Å. This investigation marked the first occasion upon which the trapping radii of deuterium at Pd dislocations had been measured, while also revealing a connection between a \( Q^{-2} \) relationship in the neutron scattering cross section and the trapping of deuterium at grain boundaries in an annealed polycrystalline sample. The existence of net neutron scattering beyond that expected within dislocations for a deformed polycrystalline sample verified that scattering also occurred due to deuterium within grain boundaries. Calculated dislocation densities for the cold worked single crystal \(((7.5 \pm 0.7) \times 10^{11} \text{dislocations/cm}^2),\)
“cycled” single crystal \((6.9 \pm 0.4) \times 10^{11}\) dislocations/cm\(^2\), and “cycled” polycrystalline \((4.2 \pm 0.8) \times 10^{11}\) dislocations/cm\(^2\) specimens were also given, and the dislocations within the “cycled” single crystal were found to be twice as long as those in the cold worked specimen \([52]\). Further refinement of these results on a single crystal specimen by Heuser and King \([55]\) led to the conclusion that the dislocation network introduced in cold worked Pd and cycled Pd must behave differently, specifically in that cycled Pd must be able to trap more H because individual stress field in a cold worked sample may be negated by the entanglement of neighboring dislocations. This study also limited the effective cutoff radius of the aforementioned Fermi-Dirac distribution to only 11 Å, implying that any H beyond this region should act as it would in the bulk material. Heuser and King \([56]\) confirmed these assertions through another set of SANS measurements, and demonstrated that reduction in the deuterium concentration occurred approximately 1.2 to 1.4 times more quickly in the cold worked sample than in the cycled sample. They also calculated the existence of an activation barrier for the trapping mechanism on the order of 0.20 eV, similar to that determined by Kirchheim in electrical resistivity measurements \([57, 58]\).

At the beginning of the 21st century, Maxelon et al. performed a series of SANS tests \([59, 60]\) that resolved differences in the expected responses between PdH\(_x\) and PdD\(_x\), albeit with the confounding effect of Porod scattering in the lowest momentum transfer regime that was later attributed to the presence of MnO within the sample \([53]\). In this set of tests, a radii of trapped hydrogen within the “Cottrell cloud” was directly measured, followed by development of a chemical potential relationship that provided a sound fit to the data assuming a dislocation density of \(2.2 \times 10^{13}\) dislocations/cm\(^2\). Around this time, Chen and Heuser performed a separate set of single crystal palladium deuteride experiments, in which the effects of concentration near the miscibility gap (the \(\alpha - \alpha'\) region) were studied with SANS for \(0.005 < |[D]/[Pd]| < 0.097\) \([61, 62]\). They were able to separate the \(Q^{-4}\) Porod’s law response from the \(Q^{-2}\) response seen upon increasing the concentration above the \(\alpha\) solubility ratio. The created \(Q^{-2}\) response was attributed the creation of small (approximately 20 Å thick) precipitate plates without a preferred orientation. Due to the formation of platelets occurring before the miscibility gap concentration is reached even though coherency is retained, it is assumed that this transition region is more indicative of a loss of coherency as larger structures form. The topic of coherency is revisited in the study performed by Heuser and Ju \([53]\), where changes in temperature were used to monitor the behavior of deuterium and hydrogen at consistent concentrations via SANS. The authors remarked that the earlier disagreement between H and D SANS response seen by Maxelon were correctly determined to be a result of the amplification of lattice strain by neutron scattering lengths of different sign. Additionally, the SANS response measured for the PdH\(_{0.0013}\) sample was representative of the formation of a hydride phase at dislocations, specifically due to adherence to Vegard’s law relating an expected lattice dilata-
tion of $f=1.1$ if the hydride phase were to form at dislocations. Although some of the implications of this body of work will be further discussed in Chapter 3, it can thus far be concluded from the SANS experiments that hydrogen favors the trap sites found within deformed Pd, especially when those trap sites take the form of dislocations created via the cycling process.

In light of the noted effects that the introduction of lattice dilatation could have on the atomic interaction potential, researchers began to take advantage of the properties of incoherent inelastic neutron scattering (IINS) shortly after the foundational QENS work was performed. Unlike coherent scattering, which yields characteristic dispersion curves and allows for insight into phonon vibration, IINS can be used to gain an average of these dispersion curves across all crystal orientations and determine the phonon density of states for a polycrystalline sample [19]. As was previously mentioned, INS can be used to investigate the vibrations of hydrogen within a Pd lattice, which was originally assumed to have a fully harmonic nature [20]. In order to understand the harmonic potential, the thought experiment of hydrogen atoms contained within the Pd lattice vibrating as if they were connected by a set of springs is proposed. As explained fully elsewhere [63], this relationship leads to a Taylor expansion of the interaction energy between two particles, relating the application of force to a particle with the expected vibration. In the harmonic formulation, it is assumed that the force and displacement of particles have a linear relationship, while the addition of higher order terms, known as anharmonicity, are needed in order to explain a non-linear relationship between the two. In terms of the resulting INS output, a harmonic potential is expected to show a uniformity in the change of energy per vibrational mode, i.e. a quantum change between energy of vibration $\Delta E$. On the other hand, an anharmonic potential leads to a nonuniform change in vibrational energies, leading to a “trumpet-like” where $\Delta E$ will decrease sequentially or a “well-like” scenario in which $\Delta E$ increases between modes. One of the first inelastic measurements on PdH$_x$ by Bergsma and Goedkoop was earlier discussed, and established that the first vibrational mode in $\alpha'$-phase PdH$_{63}$ has an $\Delta E$ of 56 meV, while a second mode started to appear faintly around 120 meV [4]. The importance of the effects of anharmonicity on the diffusive capability of interstitial H was remarked upon by Drexel et al. [64], who stated in 1976 that “The anharmonic coupling of the local mode oscillator to the host lattice phonon field and the dynamical amplitude perturbation of the host lattice atoms near an impurity atom increase with temperature, and possibly influence the diffusion properties of the hydrogen atom”. Drexel et al. reopened the INS path of study, investigating differences in the INS output as the concentration and temperature in a single-crystal sample were allowed to vary. After finding first and second harmonics of 66 and 135 meV at $[\text{H}]/[\text{Pd}]=.002$ across a range of temperatures, the concentration was changed to be within the $\alpha$ regime at $[\text{H}]/[\text{Pd}]=.0272$, yielding a much wider mode centered at 63 meV. Once lower energy modes are attributed to the vibrational density
of states (VDOS) for Pd [65], the mode broadening and reduction of energy seen as the [H] concentration increased can be explained as a result of the expansion of the Pd lattice to accommodate the forming of the hydride phase. Rush et al. [66] determined that anharmonicity is the sole cause of the deviation in the isotopic dependence of optic vibrational modes, H/D vibrations that are 180° out of phase with those of Pd due to existence of multiple atoms within the lattice basis. This result was validated by the appearance of vibrational peaks at 69, 137 and 156 meV for a Pd plate sample with three different α-phase H concentrations applied, compared to 46.5 meV for a deuterium infused sample. Using the existence of the lowest order nonlinear term in the aforementioned Taylor expansion for the interaction, they concluded that the first anharmonic mode for H should have an energy of $2\hbar \omega + 19$ meV, which at 157 meV is within experimental error of the determined value. Additionally, the assumption of a harmonic oscillator would have implied a ratio of $\omega_H/\omega_D = \sqrt{2}$, which was determined to be false. In the early 1990’s, Kolesnikov et al. decided to interrogate a Pd plate containing a high [H] at low temperature, hoping to determine how the ordered β-phase would behave. They experimentally investigated PdH sub script 99 at cold temperatures [67] and displayed that the anharmonic dependence seen by Rush et al. could potentially be described by optical phonon dispersion convoluted into the INS results, manifesting themselves in the form of a “shoulder” at higher values of energy transfer as seen in Figure 2.8. Elsässer et al. also proposed revisions to the analysis of Rush et al., using first principles calculations to suggest that the degeneracy of phonon modes in specific lattice directions were not correctly accounted for and thus a feasible intermediate peak around 115 meV was ignored [68]. Additionally, they determined that it was possible for the isotopic diffusion dependence to be directly related to the site occupation of each isotope, stating that tritium/deuterium would inhabit tetrahedral interstitial sites as the temperature was lowered significantly. Finally, it was shown theoretically by Elsässer et al. that the vibrational state of hydrogen atoms is dependent on the hydrogen concentration, as many had seen before. Ross et al. performed experimental investigation into annealed PdH sub script 99 at 25K, and it was expected that the large energy transfer window (up to 800 meV) of the applied spectrometer system would allow for validation of the IINS theory proposed by Elsässer et al. [69]. Indeed, the results found by Ross et al. as seen in Figure 2.8 demonstrated the degeneracy discussed by Elsässer et al., and furthered the discussion by determining that the potential energy in the [111] and [110] lattice directions with respect to the octahedral site must retain a parabolic shape, while the potential in the [001] direction is at first similar but then takes on much steeper increase as a direct result of approaching the nearest-neighbor Pd site. Kemali et al. [70] also built off the development of Elsässer to construct the dynamic structure factor based off incident direction for a single crystal sample using ab initio simulations, and verified that phonon degeneracy is a likely cause of the ill-defined high energy modes from earlier
tests. These simulations were validated via a set of tests performed on PdH0.85, as seen in Figure 2.8, and led this group to the conclusion that phonon degeneracy due to a potential with semi-symmetric behavior could cause anharmonic behavior. Belov et al. recently used ab initio tests to determine that the anharmonicity was due directly to the relationship between Pd-H and not due to the primarily harmonic H sublattice [71].

Besides the completed studies on annealed polycrystalline or single crystal samples already discussed, other recent studies have correlated the anharmonic nature of the deformed Pd lattice with the hydrogen trapping mechanism by performing studies on deformed samples under conditions where trapping was expected to be evident. Stuhr et al. were the first to take it upon themselves to incorporate structurally deformed Pd into INS measurements [72, 73]. Using nanocrystalline-Pd instead of the standard Pd single crystal or polycrystalline sheets, Stuhr et al. demonstrated that a peak in the energy range between 50 and 80 meV (with a center close to 65 meV) existed for a nano-PdH0.048 at both 10K and room temperature, while it did not exist at all for nano-PdH0.024. This mode is said to directly relate to the residence of hydrogen in crystalline regions of the Pd. On the other hand, the lower concentration sample shows an increased INS intensity between 90 and 130 meV, which is instead attributed to a significant buildup of hydrogen at grain boundaries due to the similarity of this peak to that for surface absorption of hydrogen [72]. Heuser et al. were the first to investigate the hydrogen trapping mechanism directly via IINS by applying the FANS instrument at NIST to a sample space near the \( \alpha - \alpha' \) transition, testing cycled (\([\text{H}]/[\text{Pd}]=0.0008\)) at 4K and 295K and annealed (\([\text{H}]/[\text{Pd}]=0.015\))
at 295K \cite{74}. In this work, a number of points were made, beginning with accounting for the increase in intensity between 50 and 80 meV originally noted by Stuhr et al. \cite{72} as a spurious effect. This effect was eliminated in future work by the introduction of a bismuth filter. Besides confirming the previous assertions for first harmonic peaks in the $\alpha$ and $\alpha'/\beta$ phases (69 meV vs. 57 meV), it was shown that deformed PdH$_{0.0008}$ exhibits a transition from an $\alpha$-type peak at 295K (66 meV) to a $\alpha'$-type peak at 4K (59.0 meV). The deviation between the deformed and annealed peak (measured at 68 meV) was then attributed to hydrogen residing within the lower strain near-core trapping sites as a result of increased thermal agitation as the hydrogen began to depopulate the expected lower temperature traps, an assertion that was supported by earlier SANS investigations. Finally, it was estimated that the local concentration of hydrogen trapped at dislocations at 295K is $[\text{H}]/[\text{Pd}]=0.12$, while the existence of the $\alpha'$-type peak at 4K indicates that almost all hydrogen is contained in trap sites. The conclusion was further supported by previously discussed SANS work by Heuser et al. \cite{53}, and also by the PhD thesis of Ju \cite{75}, where it was confirmed using the FANS and ARCS instruments at the Spallation Neutron Source (SNS) that at intermediate temperatures (100K and 200K), there was a proportional transition from a greater intensity in the $\alpha'$ phase peak to the $\alpha$ phase peak. Also, Ju pointed out that a significant trapped concentration of $[\text{H}]/[\text{Pd}]=0.2$ remains visible in the INS vibrational peak even at 200K for a PdH$_{0.00134}$ deformed sample, a concentration much below the expected $\alpha'$ formation point in annealed Pd. The $ab\ initio$ study performed by Trinkle et al. \cite{76} accompanies the FANS results, with the purpose of including effects of randomized hydrogen occupancy in dislocation core and near-core sites due to strain fields, vibration of neighboring Pd, and the anharmonic potential expected of hydrogen. They point out that due to peak broadening, it is difficult to see hydrogen trapping at the dislocation core at room temperature even though it still occurs. It is also reasoned that as temperature is lowered and a Cottrell atmosphere is formed, the local hydrogen concentration is high enough to validate the existence of hydride formation seen consistently in the SANS measurements as rod-like structures. Their results point to a full dissolution of the formed hydride phase at 300K and subsequent detrapping from dislocations, which was further validated by Heuser et al. \cite{77} in a room temperature, single crystal SANS experiment indicating a much smaller trapping radius (about 4 Å vs. 11 Å \cite{55}) and a small trapping concentration ([H]/[Pd]=0.06). It was postulated that these smaller dimensions cannot sustain optic mode dispersion due to weak, long-scale H-H interactions, thus leading to the characteristic $\alpha$ phase peak energy. Other explanations for the high energy shoulder have not yet been fully validated, such as the Frank-Condon transition discussed by Kemali et al. \cite{70} which directly correlates changes in the electronic energy state with an easier transition between vibrational states.
2.6 Diffusion in Deformed Polycrystalline Palladium

2.6.1 Insight into the Deformed Palladium Diffusion Process Via non-QENS Techniques

The aforementioned analyses of hydrogen trapping by SANS and the vibrational density of states by IINS constitute solid evidence that the phase transformation witnessed at low concentrations in low [H] deformed PdH$_x$ is likely reflective of a temperature dependent hydrogen trapping mechanism, in which hydrogen will inhabit below-core and near-core trapping sites at low temperatures while higher strain sites will be abandoned under thermal relaxation. As it happens, this detrapping occurs as the Debye temperature of the PdH$_x$ system is approached, marking this as a characteristic temperature for hydrogen VDOS to depart from the lowest energy trap state. What can this allow us to qualitatively conclude about the nature of hydrogen diffusion within such a medium, as would be indicated directly through QENS measurements? As has already been mentioned, early molecular dynamics simulations verified the existence of an O-T-O diffusion pathway in bulk crystalline PdH$_x$ as discussed in the review by Flanagan [32]. This result was further validated through more recent attempts to develop accurate embedded-atom potential interactions for Pd-H alloys, showing a residence time of 440 picoseconds at the octahedral site followed by 10 ps at the tetrahedral site [38, 78]. However, additional diffusion pathways will likely exist in a deformed sample beyond those seen in the bulk polycrystalline sample, a claim that is supported by H residency within dislocations as verified by the SANS results. Before settling into the QENS-based analysis, the literature on other experimental methods of diffusion analysis must be discussed. The basis of diffusion research within α-phase deformed PdH$_x$ is due to a series of papers by Kirchheim et al. starting from 1981. Electrochemical diffusion was applied, and demonstrated a decrease in the diffusion coefficient $D$ as the concentration decreased from [H]=10$^3$ at. ppm. to around [H]=10$^1$ at. ppm., but saw a slower decline as the lower concentration was approached [58]. Additionally, due to testing at both 295K and 322K, a larger decrease in diffusivity as a function of increased deformation was found in the lower temperature specimen. The initial decrease in diffusivity was described as an effect of deep-lying trap sites being filled and thus encouraging diffusivity amongst sites with lower energy barriers, a process slowed by decreasing the concentration as a greater ratio of the hydrogen would remain trapped in sites with larger barriers. However, the divergence seen as the concentration was significantly lowered was attributed to dislocation pipe diffusion, as the expected trap sites at the core would become desaturated and would allow for such a behavior. Kirchheim then progressed to a more quantitative discussion. A model for the chemical potential and an experimental value for the enthalpy of hydride formation within a
dislocation were applied to a Fermi-Dirac function dependent on concentration, and the conclusion was drawn that the interaction energy had an $r$-dependent component related to induced stress, as well as a constant saddle point energy necessary for hydride formation\cite{57}. This line of reasoning also determined that at certain concentrations, the experimental chemical potential would identically match the theoretical Fermi energy of the system. The following year, Kirchheim et al. elaborated on this concept, establishing that the energy potential of available hydrogen sites could be described as a continuous, Gaussian function of the free enthalpy, which in turn implies that site occupancy operates similarly to electrons in metals until the Fermi level is reached\cite{79}. Effectively, this setup assumes variation in the trap energies, but the intermediate saddle points between them are assumed to have a constant reference energy. As seen in Figure 2.9, this allowed for a development of the net flux and the effective diffusivity, which are shown to be directly proportional to the diffusion constant, the average trapping energy, and the concentration\cite{80}. The nuances of this effective diffusivity will be elaborated upon in Chapter 3. This array of tests did not take into account differences that would be seen at other temperatures, and the tests were performed on cold worked specimens, which do not have comparable dislocation arrays to cycled samples as previously discussed. Importantly, it was noted that the systematically larger values seen at low concentrations ($<10^2$ at. ppm.) could be due to enhanced diffusivity along dislocation cores \cite{80}. Further measurements by Rodrigues and Kirchheim et al. used the same approach for describing the diffusivity, characterizing the distribution of site energies with a Gaussian of width 0.155 eV/atom and a difference between the average site energy versus the saddle point energy of 0.021 eV/atom\cite{81, 82}. It was proposed that low energy sites are relatively large, leading to low saddle point energies. Therefore, a relationship occurs between the saddle point energy and nearest neighbor sites, explaining why hydrogen will want to jump into these sites until they are filled.

In 2003, Gapontsev and Kondrat'ev\cite{83} created a review of Kirchheim’s model, as well as a further extension of another preexisting model created by Brouwer et al.\cite{84} in an effort to macroscopically describe hydrogen diffusion in Nb-V alloys. The implications of this review bear need for further discussion. In the model developed by Brouwer et al., it was determined that for BCC alloys such as Nb$_{1-y}$V$_y$, it is possible to create a more accurate model for interstitial hydrogen diffusion by considering the possibility of site blocking as well as site-dependent saddle point energies. By proposing site blocking, Brouwer’s model required the introduction of probabilities for nearest neighbor sites in a binary alloy, and also introduced other parameters relating the likelihood of such configurations. As will be further elucidated upon in the following chapter, the work of Gapontsev and Kondrat’ev attempted to deter the overuse of parameters, opting instead to develop a setup purely dependent on the concentration and diffusive properties of each pure element contained in the disordered alloy.
Figure 2.9: Diffusivity in deformed Pd at various concentrations between $10^4$ and $10^1$ at. ppm., fit to the theoretical basis of Kirchheim dictating a dependence of diffusivity on the concentration. All tests were performed at 295K, which inhibits insight into effects of temperature [80].

While impressive in terms of experimental agreement for binary alloys, the efforts of Gapontsev and Brouwer are more applicable to disordered alloys, not deformed systems, i.e. there is no inherent mechanism accounting for the dislocations introduced by hydride cycling but rather for substitutional impurities related to binary alloy concentration. As a result, the model developed by Kirchheim et al. is likely the best description available for the expected deformed Pd-H interaction, with the addition of consideration for H-H interaction within dislocations.

### 2.6.2 Beyond Chudley-Elliot: A Search for a Quantitative Validation of Deformed PdH Diffusion using QENS

Thus far, the Chudley-Elliot model has been established as a useful bounds for the description of QENS diffusivity results for a Bravais FCC lattice. However, as has already been shown deformed α phase PdH$_x$ is far from having such
uniformity. By establishing how the concentration-dependent hydrogen trapping mechanism functions via a Cottrell atmosphere, and how this mechanism leads to site-dependent activation energies and selective blocking, the necessary foundation has been laid in order to critically approach the current breadth of diffusion results using QENS in deformed PdH_x. The first direct measurement of diffusivity in deformed PdH_x was performed by Stuhr and Janssen et al. [85, 86] on nanocrystalline PdH samples similar to those used in earlier INS measurements. Two different nanocrystal types were tested, and the samples were tested between 220K-300K with [H]/[Pd] set to 2.9 or 3.7 at. % respectively. These concentrations were used to ensure that the traps within dislocations inside the grains were fully saturated such that diffusion along grain boundaries would be the predominant process besides bulk diffusion. The method of analysis used here is important to note, because these works applied two neutron spectrometers at the Institut Laue-Langevin with differing instrumental resolutions (the IN16 backscattering spectrometer with resolution of around 0.6 µeV and the time-of-flight spectrometer IN5 with resolution of 60 µeV) in order to independently characterize the different rates of diffusion expected. It bears noting that although there is no mention of the incident neutron energy, the displayed results demonstrated an accessible energy transfer window on the meV scale for IN5, while IN16 is on the tens of µeV scale. Stuhr and Janssen et al. used the earlier results of Völkli and Alefeld and the Chudley-Elliot model to establish that the characteristic Lorentzian width for Q=1.01 Å would be close to 2.6 µeV for bulk hydrogen diffusion at 288K. The IN16 result seen in Figure 2.10 for this parameter set was found to have a Lorentzian width of 3.3 ± 0.6 µeV, falling within experimental error of this value. This broadening would appear in the result from the other spectrometer as well, except that it has significantly poorer resolution than this first Lorentzian’s width. Stuhr and Janssen make an important distinction here, acknowledging that a narrow peak width will appear only as a contribution to the elastic peak on the lower resolution IN5 instrument, while any broad components would only appear as contributions to the constant background intrinsic to the IN16 instrument. As is seen in Figure 2.10 it is necessary to fit the data from IN5 using a sum of two Lorentzians added to the elastic component. At Q=1.24 Å, two Lorentzian widths of 22 µeV and 400 µeV are accounted for. Stuhr and Janssen et al. correlated the output seen from the IN16 spectrometer with a bulk diffusion process occurring within the nanocrystals. They attributed the significantly larger width seen to enhanced diffusion along grain boundaries, acknowledging that the QENS component intensity increased with increasing Q as is typical of a locally restricted diffusion process. Although this work demonstrated that different spectrometers could be used to determine unique diffusion rates within a deformed medium, further analysis beyond this semi-quantitative comparison of the broadening is lacking, and insufficient data was gathered towards ascertaining a temperature dependence of the diffusive mechanism. Also, Stuhr and Janssen did not expect
to see the effects of DPD here, as a higher hydrogen concentration was used to ensure that the goal of characterizing grain boundary diffusion was met.

Figure 2.10: QENS peaks obtained via two separate spectrometers, the IN5 time-of-flight spectrometer (top image) and the IN16 backscattering instrument (bottom image). Two Lorentzian curves were necessary to properly describe the data from the wider resolution IN5 spectrometer, while a single Lorentzian characterized the IN16 behavior. At the tested $[\text{H}]$, the wider Lorentzian peak on IN5 is attributed to grain boundary diffusion [85, 86].

The current investigation has been directly motivated by the work of Heuser et al. [12] in 2014, who for the first time applied the QENS method to a deformed PdH$_x$ system at low concentrations in order to directly quantify the diffusion behavior as a function of temperature, without relying upon the indirect chemical diffusion or transport model methods used previously. Using cold-worked polycrystalline Pd sheets of high purity, the sample material was cycled across the $\alpha - \alpha'$ miscibility gap in order to introduce dislocations as previously described, followed by the hydrogen concentration being lowered to $[\text{H}]/[\text{Pd}]=1100$ at. ppm. and $[\text{H}]/[\text{Pd}]=520$ at. ppm in two samples sets in an effort to capture enhanced diffusivity along dislocations while negating the trapping seen at higher concentrations. Two instruments were used for the analysis, namely the neutron backscattering silicon spectrometer (BASIS) at Oak Ridge National Laboratory and the high-flux backscattering spectrometer at NIST, with an annealed sample at $[\text{H}]/[\text{Pd}]=2020$ at. ppm. used to create a comparable reference of the deformed results to the bulk diffusion properties. With instrumental res-
olutions of approximately 3.4\,\mu eV and 1\,\mu eV respectively, this study was tasked with evaluating the diffusivity of hydrogen at temperatures between 150K-400K. Within this range of temperatures, it was expected that the detrapping temperature of approximately 300K postulated earlier \cite{76} would be witnessed, in addition to an effect due to the formation of a hydride phase in deformed samples below 250K as seen in the earlier IINS and SANS results. Although some of the results found from this study will be further reviewed in Chapter 5, the methods and base results obtained will be elaborated upon here. Assuming the use of a single or dual set of Lorentzian functions in order to classify the QENS broadening, the isotropically averaged Chudley-Elliot model was applied to the obtained data. By applying an Arrhenius relationship to the determined diffusivities, characteristic values of $D_0=0.005 \pm 0.004 \, \text{cm}^2\text{sec}^{-1}$ and $E_a=0.23 \pm 0.02 \, \text{eV}$ were found, yielding a strong correlation to the results compiled by Vökl and Alefeld. For the deformed sample, a single Lorentzian was seen to classify the broadening at temperatures above 300K where bulk diffusion is expected to dominate, while at lower temperatures two Lorentzians provided a better fit. In this study, the broader QENS component seen had comparable width to the energy transfer window accessible to the spectrometer, which as pointed out by Stuhl and Janssen et al. makes it difficult to distinguish this broadening from a constant energy background. Thus, the narrower component was primarily used to quantify the QENS broadening at these temperatures. Characteristic values were obtained using an Arrhenius relationship, resulting in $D_0 = 9(\pm 3) \times 10^{-6}$ and $10(\pm 5) \times 10^{-6} \, \text{cm}^2\text{sec}^{-1}$ whereas $E_a=0.083 \pm 0.005 \, \text{eV} \, \text{atom}^{-1}$ and $0.042 \pm 0.012 \, \text{eV} \, \text{atom}^{-1}$, corresponding to $[\text{H}]/[\text{Pd}]=1100$ at. ppm. and $[\text{H}]/[\text{Pd}]=520$ at. ppm respectively. This data is graphically depicted in Figure 2.11 with the variation in $E_a$ and $D_0$ clearly evident. As is pointed out, the significant reduction in the absolute diffusion coefficient cannot be attributed to site blocking within bulk diffusion sites, as previous results have shown that this value will remain essentially consistent in a test using high concentration samples. Since it was also shown that diffusion within a PdH hydride will remain consistent with bulk diffusion \cite{87}, it was determined that the $D_0$ values found must be indicative of site blocking occurring within core sites or near-core sites, validating the existence of hydrogen DPD in the system. From this conclusion, the concentration and temperature dependence were discussed. The results showed that the diffusivity above 300K was reflective of the bulk diffusivity of the annealed sample at these temperatures, effectively verifying detrapping mechanism. Also, a decrease in concentration led to a decrease in activation energy, which was reasoned to be a result of a higher sampling of jumps between sites under higher lattice strain when less site blocking could occur, leading to a lower activation energy due to the dampening of the jump barrier induced by the lattice strain. These observed values were then analyzed in the context of \textit{ab initio} simulations of a single hydrogen contained within a Pd edge dislocation superstructure, and a model for the expected diffusion mechanism was proposed as is shown in Figure
It was suggested that hydrogen will favor trapping sites below the inserted half plane of the dislocation, and that these octahedral-tetrahedral trap sites are directly connected to metastable, asymmetric sites within the core. It was then expected that hydrogen will undergo jumps characteristic of the activation energy for DPD within these core sites, until finding another available trap site below the core. By postulating that the metastable DPD core sites were only connected to trap sites and could not access the bulk octahedral sites, Heuser et al. provided an explanation for the reduced $D_0$ value for DPD, attributing it to the lower possibility of DPD jumps occurring versus jumps from the trap sites to the bulk octahedral sites.

Figure 2.11: Direct determination of the hydrogen DPD mechanism in Pd led to an Arrhenius temperature scheme that was used to determine the activation energy and absolute diffusion coefficient for deformed and annealed Pd, as shown in the left image. The lower concentration data has a lower activation energy, implying that DPD may be occurring but is then inhibited at higher [H] due to site blocking [12]. The right image demonstrates the anomalous behavior of the jump length seen due to fitting the Chudley-Elliot model to the QENS peak broadening [88].

While this result from Heuser et al. seemed to fully verify the existence of DPD at sufficiently low [H] and temperature, some aspects of this work were left unresolved by the conclusions drawn. Firstly, this work did not give consideration to the expected distribution of trapping energies as postulated by Kirchheim’s model nor did it quantitatively account for the effects of site blocking per Brouwer’s concept, which could easily provide more quantitatively relatable results for the concentration dependence of the activation energy. Secondly, as pointed out in the supplemental material for this work [88], Heuser et al. acknowledged an anomalous effect in the calculated jump lengths obtained from the Chudley-Elliot model; instead of seeing a consistent jump length close to the octahedral-octahedral distance of 2.75 Å as expected, an increased jump length from near 2.8 Å at 200K to nearly 3.5 Å at 300K was observed in the higher [H] samples. This statistically significant difference became the subject of study for Schiavone et al. in a recent publication [89], along with other aspects of the experimental analysis. In this ab initio study, the authors investigated the
validity of using the Chudley-Elliot model to describe the QENS broadening in the incoherent dynamic structure factor, applying DFT to determine trapping site energies and barriers for H in edge dislocations in Pd for the first time. This study was calibrated by finding the lattice parameter and bulk diffusivity, which were shown to be L=3.852 Å and \(E_{OT}=0.277\) eV where \(E_{OT}\) is the activation energy from a octahedral-tetrahedral jump and is in accordance with previous results. For the dislocation geometry, a 382-atom Pd edge dislocation with one hydrogen atom is established, first by inducing a Burger’s vector of \([\overline{1}10]\) while applying periodic boundary conditions in the \([1 \overline{1}2]\) threading direction, then allowing this geometry to relax and form partial dislocation core geometry.

Assigning known values for dislocation energy and H interstitial-dislocation interaction, two activation energies are established. Below the core region, there is a lower activation barrier of 0.151 eV seen, while a pathway inside the partial core is found to be 0.111 eV, both values that are much lower than the experimentally measured activation energies. These values are said to be relative to the previously determined ground state H in an octahedral site below a partial core of -0.125 eV. Schiavone et al. also determined the geometry of these pathways, comparing the path along the threading direction below and within the partial core to that of the bulk Pd, shown explicitly in Figure 2.13 [89].

Interestingly, although the pathway below the partial core is expanded due
Figure 2.13: *Ab initio* calculated strain fields for the octahedral and tetrahedral interstitial sites that have been exposed to an edge dislocation with a Burger’s vector pointing along $\frac{3}{2} [110]$. After relaxation, the dislocation dissociated into two partials, leading to the two core structure seen. The red region indicates tensile strain, which is at its largest immediately below the formed partial cores, making this site a good candidate for hydrogen trapping and enhanced diffusivity [89].

to volumetric strain, it appears that the structure remains identical to the octahedral-tetrahedral site distribution seen in bulk. On the other hand, due to the existence of a hexagonal close packed stacking fault orientation, the region between the hcp and fcc structures leads to sites without octahedral or tetrahedral symmetry, instead appearing to host two sites within a space analogous to an octahedron. These novel sites demonstrate an energy of 0.03-0.06 eV above the tested ground state. In context of the Cottrell atmosphere theory, the diffusion barriers below the core into the core as well as out of the core itself are found to be low, about .04 eV for each. Schiavone et al. then take a step in the direction of Kirchheim’s theory, acknowledging that a distribution of trapping energies must occur surrounding a dislocation, but decide to use an approximation to the site energy distribution instead of calculating each site independently. Using a linear approximation of the site energy in bulk and at $\pm 2\%$ strained bulk Pd, the observed strain rate in the simulated dislocation model are applied to find jump rates between sites. The determined jump rates and site energies for core and near-core geometry are then applied to a kinetic Monte Carlo (KMC) model, determining an “effective” activation barrier of $E_a=0.125$ eV for the region between 100-500K. As hinted at by the author, assessing DPD up to 500K causes a deviation from linearity in the Arrhenius data. This has already been discussed previously, since the hydrogen depopulation from expected trap sites will likely occur near the temperature of 300K, and thus assessing DPD beyond this threshold will lead to skewed values. The authors assert that the average jump distance seen does not vary, which may be a symptom of the application of the KMC method since the jump vectors collected through DFT may not correctly reflect the temperature effects upon the partial core structure. Proceeding from the DFT analysis, the authors moved to assess the discrepancy in jump length found by Heuser et al. due to their use...
of a single or double Lorentzian to characterize a process incorporating a distribution of site energies. A functional form of the incoherent dynamic structure factor is established, taking the form

$$S_{\text{inc}}(\mathbf{Q}, \omega) = \frac{1}{\pi \hbar} \sum_{i=1}^{N_{\text{sites}}} w_i(\mathbf{Q}) \frac{-\tilde{\lambda}_i(\mathbf{Q})}{|\lambda_i(\mathbf{Q})|^2 + \omega^2} ,$$

(2.4)

representing a sum of Lorentzians whose widths and weights \(w_i\) are derived from the eigenvalues \(\tilde{\lambda}_i\) of the Hermitian jump matrix. The Hermitian jump matrix form is a direct result of the jump matrix in reciprocal space, stated as

$$\Lambda_{mn}(\mathbf{Q}) = \nu_{mn} \exp(i\mathbf{Q} \cdot \mathbf{s}_{mn}) - \delta_{mn} \sum_{l \neq n} \nu_{nl},$$

(2.5)

where \(\nu_{mn}\) is the jump rate between two sites \(m\) and \(n\), while \(s_{nm}\) represents the jump vector between sites \(n\) and \(m\). While this can be further discussed in Chapter 3, the implications of this model are that both the widths of the summed Lorentzians and their fractional contribution to the overall peak broadening can be determined via the performed simulations. An additional assumption to be noted is that the jumps are assumed to be discrete events, yielding discrete site energies and jump rates due to the relative periodicity of the lattice structure. The authors attest that a further step must be taken for the model to be applicable in a polycrystalline sample, which will introduce a simple relation when the Bravais lattice form is assumed but leads to a spherical average of Equation 2.4, namely

$$S_{\text{inc}}(Q, \omega) = \frac{1}{\pi \hbar} \int_0^{\inf} W(Q; \lambda) \frac{-\tilde{\lambda}}{\lambda^2 + \omega^2} .$$

(2.6)

Equation 2.6 relates the expected form of the spherically averaged incoherent dynamic structure factor for polycrystalline deformed PdH_x as a function of a density of states for the weights \(W(Q; \lambda)\). Equation 2.6 would accordingly reduce to a Lorentzian of a single width if this density of states is assumed to be a Kronecker delta function, thereby eliminating its contribution to the peak width. The use of this function leads to an impressive development, due to the model’s capability to correctly account for variability within polycrystalline jumps originally noted in the different forms of the Chudley-Elliot model used in the work of Rowe et al. [41]. Comparing Figure 2.5 with Figure 2.14 from Schiavone et al. demonstrates that although the Bravais lattice approximation is acceptable at low Q values, the density of jump rates \(W(Q; \lambda)\) yields a significant variation from the older form. Since the darkest grey region of the image depicts the region where the density of jump rates approaches 1, equivalent to a single Lorentzian mode, the C-E model underestimates the rates at the region closest to what it was expected to model.

Using this model, Schiavone et al. then addressed directly the discrepancy of the results seen by Heuser et al. in the context of the QENS instrument.
Figure 2.14: Comparison of the Chudley-Elliot form for [111] and [110] as well as the polycrystalline approximation with the spherically averaged density of rates technique developed by Schiavone et al., with the weight of each contributing width indicated using gray scale. It is obvious that at larger \( \vec{Q} \), the original C-E model fails to represent the range of rates possible. [89]

utilized primarily, the BASIS instrument at ORNL. Using single values for the experimental resolution and experimental window of the instrument (3.4 \( \mu eV \) and 100 \( \mu eV \) respectively), a least squares fit of \( S_{inc}(Q,\omega) \) for the experimental range \([3.4,100]\), denoted as \( \Gamma_{log,[3.4,100]} \), was performed and compared to a least squares fit of the entire range of widths possible over the energy transfer range \([0,\inf]\). From this analysis, another detraction from the validity of the original C-E analysis is noted. Both the weighted Lorentzian fits and an estimate to the C-E model for this Lorentzian sum are shown to fit well to the experimental fits but do not at all capture the physical rates expected for the full range of energies for \( S_{inc}(Q,\omega) \). Using the \( \Gamma_{log,[3.4,100]} \), it was shown that an activation energy of \( E_a=0.068 \text{ eV} \) would be obtained; additionally, the experimental least squares fit importantly suggest that the increase in jump length is not due to a geometrical anomaly within the core, but rather is an artifact of not properly weighting the Lorentzian fits in the original analysis of the data. In summary, Schiavone et al. note that the Chudley-Elliot model will provide an obvious oversimplification of the incoherent dynamic structure factor, and will lead to a model in which Lorentzian widths can lead to an Arrhenius fit for an activation energy while the only outlier from the model is found in the distorted jump length.

This paper gives a comprehensive insight into the true workings of hydrogen diffusion within dislocations, but leaves some room for contemplation. Firstly, due to the nature of DFT simulations, it is not possible to study the effects of additional hydrogen introduced into the system, and as a result the effect of H-H interactions and hydride formation below and within the core must be ne-
glected. It is feasible that the formation of these structures below the core could lead to more enhanced diffusivity and lower activation energy at higher concentrations, due to a reduction of the barrier in the below core-inner core pathway, but this investigation was outside the scope of the authors’ work. Secondly, this work fails to address the possibility of departure from DFT simulated results when the slower relaxation times of bulk diffusivity are incorporated with those seen in the dislocation core, addressing these concerns independently. However, for any experimental test performed near 300K, it is feasible to suggest that there is a thermal dependence of the ratio of bulk-like and core-like jump rates. This distinction will be further addressed in the current work in the context of an expanded range of experimental QENS data. Finally, though complicated and time intensive to apply, the discrete weighted jump rate model suggested does not accurately reflect the continuous Gaussian distribution of site energies postulated by Kirchheim et al., which likely could be produced using a simpler model assuming a continuous distribution of jump rates. In their Monte Carlo assessment of 2000, Hua et al. originally pointed to the concern that using a Lorentzian fit to explain the QENS broadening would not accurately model $S_{\text{inc}}(\tilde{Q}, \omega)$, and also introduced data for the intermediate scattering function (ISF) of the disordered metal-hydrogen system. The intermediate scattering function will be a key point of analysis in this work, and can be for now established as the inverse Fourier transform of $S_{\text{inc}}(\tilde{Q}, \omega)$, represented as $F(\tilde{Q}, t)$. Hua et al. present the ISF in brief, and point out that an exponential fit (the inverse Fourier transform of a Lorentzian) does not correctly model the data. Instead, the decay seems to take on a stretched form. This sort of stretched exponential form has been seen in research performed by Swenson et al. on the QENS broadening seen for experiments done to test water dynamics. This form can be said to take into account the continuum nature of postulated site energies, and thus an extension of this mode of analysis to investigate the deformed PdH$_x$ system will be postulated in Chapter 3. As the debate over how to properly assess the diffusivity of hydrogen within a deformed Pd matrix continues, it is hoped that the research presented in this work takes another step in the correct direction. In light of the research already performed, this work will use the results obtained from QENS instruments of varying instrumental resolution and energy transfer window in order to more accurately assess the full range of diffusive action in deformed PdH$_x$. The applicability of the original Chudley-Elliot model to the results obtained will be discussed, in addition to methods for simultaneously comparing the results obtained from different spectrometers. While the recent work by Kofu et al. probes the bulk PdH$_{0.73}$ and nanocrystalline PdH$_{0.47}$ systems using three different neutron scattering techniques, their presented results are analyzed independently for each instrument. However, their results give promise to the possibility of multiple Lorentzian analysis within the PdH$_x$ system, since two distinct Lorentzians were seen within the bulk PdH$_x$ sample on the instrument with a larger energy transfer window while a single
Lorenztian was noted on the backscattering spectrometer results. This work will display that the use of the combined intermediate scattering function instead of independently analyzing the dynamic structure factor for each instrument allows for a clearer picture of diffusion within a “cycled” deformed Pd sample due to the postulated variation in dislocation site structure.
Chapter 3

Theoretical Models

3.1 Neutron Scattering

The basis of neutron scattering analysis is the neutron scattering cross section. While it is possible to classify the scattering cross section on a macroscopic scale using the linear attenuation coefficient, the microscopic scattering cross section $\sigma$ is utilized in neutron scattering because it relates directly the expected response of a scattering system to neutrons of a specified energy and direction. The microscopic scattering cross section is typically represented in terms of barns, equivalent to $10^{-24}$ cm$^2$, where the dimensions of the cross section point to the effective spatial region in which an incident neutron should undergo a scattering event. This simple definition does not hold true when variability in the incident neutrons is considered, and thus it is common to describe $\sigma$ as the interaction probability per unit path length that has been normalized to a single target atom per unit volume, leading to units of $1/cm^3$. It is typical to represent $\sigma$ with a more useful format known as the double differential cross section, $\frac{\partial^2\sigma}{\partial\Omega \partial E}$, which provides the probability that a neutron with a known incident energy $E_i$ will scatter from the sample within the solid angle $d\Omega$ around $\Omega$ and exchange energy to the system between $\Delta E = E_i - E_f$ and $\Delta E + dE$. As earlier discussed, the distinction between an elastic and an inelastic scattering event is made based on whether energy is conserved by the neutron or lost upon scattering. In addition to these classifications, two different scattering modes known as coherent and incoherent scattering will be factored into the double differential cross section. Coherent and incoherent scattering differ in that coherent scattering reflects collective atomic motion as a result of constructive interference between the scattering neutrons, while incoherent scattering does not relate structural information. Incoherent scattering provides information on position changes for a single scattering nuclei over time, in contrast to coherent scattering which yields a paired correlation of relative position change between nuclei. The large incoherent scattering cross section of the H nuclei relative to metals it has been absorbed within lead to the conclusion that incoherent scattering is an ideal technique for studying the transport of H within metals. In order to perform neutron spectroscopy, the double differential cross section will be split into a sum of coherent and incoherent components. As it is of central
interest to QENS studies, the incoherent component alone can be written as

\[
\frac{\partial^2 \sigma_s}{\partial \Omega \partial E} = \frac{\sigma_{inc}}{4\pi} \frac{k_f}{\hbar N} S_{inc}^\alpha(\vec{Q}, E), \tag{3.1}
\]

where \(\sigma_{inc}\) is the incoherent scattering cross section and is equivalent to \(4\pi(\bar{b}^2 - \langle \bar{b} \rangle^2)\), namely the root mean square deviation from the average neutron scattering length \(\bar{b}\). Scaling by the ratio of the initial and final wavelengths for the scattered neutrons thus yields \(S_{inc}^\alpha(\vec{Q}, E)\), known as the incoherent scattering law or the incoherent dynamic structure factor. Equation (3.1) can be modified to yield a relationship to the angular frequency instead of energy transferred by multiplying the incoherent dynamic structure factor by \(\hbar\), yielding a function of the form \(S_{inc}^\alpha(\vec{Q}, \omega)\). The incoherent scattering law is tied to the physical nature of the scattering system in the following way. When incoherent scattering is considered for only a single species, the incoherent dynamic structure factor can be written as a Fourier transform in the time domain:

\[
S_{inc}(\vec{Q}, E) = \frac{1}{2\pi} \int_{-\infty}^{\infty} I_{inc}(\vec{Q}, t) \exp(-i\omega t) dt, \tag{3.2}
\]

where the function given by \(I_{inc}\) is known as the incoherent intermediate scattering function (ISF) and can be described with the relationship (11):

\[
I_{inc}(\vec{Q}, t) = \frac{1}{N} \sum_i \exp\{-i\vec{Q} \cdot \vec{R}_i(0)\} \exp\{i\vec{Q} \cdot \vec{R}_i(t)\}. \tag{3.3}
\]

The physical significance of this line of reasoning becomes clearer if a return to real space from reciprocal space is made via a spatial Fourier transform of the ISF, yielding the van Hove self-correlation function \(G(\vec{r}, t)\). This function uses the relationship of each atom to the collective structure through the microscopic particle density operator \((\rho(\vec{r}, t) = \sum_i \delta(\vec{r} - \vec{R}_i(t)))\) to create a physical function describing how each atom translates in relation to its own starting position as well as the positions of the other atoms at time \(t\). In an isotropic sample, \(G(\vec{r}, t)\) provides a time dependent version of the radial distribution function. As a note, the intermediate scattering function is represented in literature using both \(F_{inc}(\vec{Q}, t)\) and \(I_{inc}(\vec{Q}, t)\). In order to avoid confusion, \(F_{inc}(\vec{Q}, t)\) will be utilized to describe the ISF resulting solely from the expected QENS response of a system, while \(I_{inc}(\vec{Q}, t)\) will indicate the unrefined intensity function derived from the direct temporal Fourier transform of \(S_{inc}(\vec{Q}, E)\) before any considerations are given to background or instrumental resolution. In the following section, the concept of the incoherent dynamic structure factor will be further expanded upon, with an explanation of how it quantitatively describes the experimentally measured QENS broadening in the context of the Chudley-Elliot model.
3.1.1 Development of Chudley-Elliot Model

The first QENS studies were performed using liquid systems, in which a difference in concentration between two volumes leads to a flow of atoms acting to remedy the imbalance. The flow occurs at a proportional rate known as the diffusion coefficient $D$. Thus, the time rate of change of concentration is proportional to the shifting concentration due to flow within a volume, as per the relationship known as Fick’s Law:

$$D \nabla^2 G_{inc}(\vec{r}, t) = \frac{\partial}{\partial t} G_{inc}(\vec{r}, t)$$  \hspace{1cm} (3.4)

where $G_{inc}$ describes the possibility of existence of a single atom at $\vec{r}$ for time $t$. This function relates the macroscopic properties of the system to the microscopic motion of the liquid’s atoms by assuming a continuous (Brownian) diffusion model, in which it is assumed that the path length between particle collisions is small enough to be considered infinitesimal compared to the system size. It can be easily shown via a spatial and subsequently a temporal Fourier transform how the ISF and incoherent dynamic structure factor manifest themselves:

$$F_{inc}(\vec{Q}, t) = \exp(-DQ^2t),$$  \hspace{1cm} (3.5)

$$S_{inc}(\vec{Q}, E) = \frac{\hbar}{\pi} \frac{DQ^2}{\omega^2 + (DQ^2)^2}.$$

The incoherent dynamic structure factor shown in Equation 3.6 assumes the form of a Lorentzian function with a characteristic half width at half maximum of $DQ^2$, implying a direct relationship between the energy and momentum transfer as well as a simplistic model for determining the diffusion coefficient. This rule can be applied only in select circumstances due to the need to fulfill the Brownian motion condition, and thus can only be directly applied to crystalline systems at small values of $Q$ and $E$. Improvements to this model were proposed by Chudley and Elliot \cite{3} in order to accommodate a divergence from the $DQ^2$ law when larger momentum transfer is considered. In their model, the Frenkel model for a quasicrystalline liquid near its melting point is considered, in which the atomic motion is generally constrained to thermal oscillation at a lattice site but will undergo a jump from one lattice site to another after a certain time of residence. In their model, Chudley and Elliot calculated that the residence time would be significantly larger than the time scale for the jump to occur, and as a result decided to neglect the duration of the jump from their model. As described in Chapter 2, the Chudley-Elliot model became the foundational concept for jump diffusion of hydrogen on a Bravais lattice, as it allows for a description of diffusion via motion of a discrete length. Many authors performing early QENS work upon PdH$_x$ systems \cite{40, 37, 41, 42, 87, 64, 43} adapted the following interpretation in order to classify the diffusive action of hydrogen in bulk Pd,
and have also modified the concept to fit different situations. The basis for the Chudley-Elliot model is the van Hove self-correlation function $G_{\text{inc}}(\vec{r}, t)$ for the system, which gives the probability of finding particles at certain positions as

$$\frac{\partial}{\partial t} G_{\text{inc}}(\vec{r}, t) = \frac{1}{n\tau_{\text{res}}} \sum_{i} [G_{\text{inc}}(\vec{r} + \vec{L}_{i}, t) - G_{\text{inc}}(\vec{r}, t)],$$  \hspace{1cm} (3.7)

which presents a discrete sum of $n$ possible directions for finding a nearest neighbor site that is a vector $\vec{L}_{i}$ from the initial site, where $\tau_{\text{res}}$ is the residence time between instantaneous jumps. Taking a spatial Fourier transform yields the intermediate scattering function for Bravais lattice jump diffusion,

$$F_{\text{inc}}(\vec{Q}, t) = F_{\text{inc}}(\vec{Q}, 0) \exp[-\Delta \omega(\vec{Q})t],$$  \hspace{1cm} (3.8)

where the term $\Delta \omega(\vec{Q})$ is a decay constant for the exponential equivalent to a summation of the probability of occurrence for each jump vector:

$$\Delta \omega(\vec{Q}) = \frac{1}{n\tau_{\text{res}}} \sum_{i} [1 - \exp(-i\vec{Q} \cdot \vec{L}_{i})].$$  \hspace{1cm} (3.9)

In the formulation for Equation 3.8, the boundary condition that the self-correlation function will be a delta function at $t=0$ is generally applied, leading to $F_{\text{inc}}(\vec{Q}, 0) = 1$ in this case. It should be noted here that when the intermediate scattering function is explicitly calculated, it is frequently represented using the form

$$F_{\text{inc}}(\vec{Q}, t) = F_{\text{inc}}(\vec{Q}, 0) \exp[-t/\tau],$$  \hspace{1cm} (3.10)

where $\tau$ is distinct from the residence time $\tau_{\text{res}}$ and describes the relaxation process for the ISF in units of time. Proceeding towards the incoherent dynamic structure factor requires caution, as different distinctions have been made for correct representations by both Bée [11] and Sköld and Nelin [87]. These different forms arose from confusion over whether $\Delta \omega(\vec{Q})$ is representative of a linear or angular frequency. A short corrected derivation is provided here, using Equation 3.8 as the origin point where $F_{\text{inc}}(\vec{Q}, 0) = F_{0}$:

$$\mathcal{F}(F_{0} \exp[-\Delta \omega(\vec{Q})t]) = \int_{-\infty}^{\infty} F_{0} \exp[-\Delta \omega(\vec{Q})|t|] \exp(-i\omega t) dt$$  \hspace{1cm} (3.11)
\[
\begin{align*}
&= \int_{-\infty}^{0} F_0 \exp[\Delta \omega(\vec{Q})|t|] \exp(-i\omega t)dt + \int_{0}^{\infty} F_0 \exp[-\Delta \omega(\vec{Q})|t|] \exp(-i\omega t)dt \\
&= F_0 \left( \frac{1}{\Delta \omega(\vec{Q}) - i\omega} - 0 \right) + \left( 0 - \frac{1}{-\Delta \omega(\vec{Q}) - i\omega} \right) \\
&= F_0 \left( \frac{1}{\Delta \omega(\vec{Q}) - i\omega} + \frac{1}{\Delta \omega(\vec{Q}) + i\omega} \right)
\end{align*}
\]

\[
\therefore \mathcal{F}(F_0 \exp[-\Delta \omega(\vec{Q})t]) = S_{inc}(\vec{Q}, \omega) = F_0 \left( \frac{2\Delta \omega(\vec{Q})}{(\Delta \omega(\vec{Q}))^2 + \omega^2} \right)
\]

The result of Equation 3.12 details the dynamic structure factor found if it is assumed that the characteristic width \(\Delta \omega(\vec{Q})\) is an angular frequency, allowing for a direct relationship between \(t\) and \(\omega\). However, Béé [11] provides a different solution for the dynamic structure factor in Equation 5.34, namely

\[
S_{inc}(\vec{Q}, \omega) = \frac{1}{\pi} \frac{\Delta \omega(\vec{Q})}{(\Delta \omega(\vec{Q}))^2 + \omega^2},
\]

which does not equal the result of Equation 3.12. In actuality, a small modification of the derived result displays the intended result of Béé. Assuming that the angular frequency and linear frequency are related by \(\omega = 2\pi f\) and that a similar relationship exists for the characteristic HWHM,

\[
S_{inc}(\vec{Q}, \omega) = F_0 \left( \frac{2\Delta \omega(\vec{Q})}{(\Delta \omega(\vec{Q}))^2 + \omega^2} \right) \rightarrow S_{inc}(\vec{Q}, f) = F_0 \left( \frac{2(2\pi \Delta f(\vec{Q}))}{(2\pi \Delta f(\vec{Q}))^2 + (2\pi f)^2} \right)
\]

\[
\therefore S_{inc}(\vec{Q}, f) = \frac{1}{\pi} \frac{\Delta f(\vec{Q})}{(\Delta f(\vec{Q}))^2 + f^2},
\]

which matches the form postulated by Béé. It seems that in this case, the \(\Delta \omega(\vec{Q})\) was used somewhat erroneously, as the Lorentzian form presented is for that of linear frequency instead angular frequency. In the case of Sköld and Nelin, a version of the dynamic structure factor using linear frequency was applied:

\[
S_{inc}(\vec{Q}, \nu) = \frac{f(\vec{Q})}{(f(\vec{Q}))^2 + 4\pi^2 \nu^2} \Delta \nu(\vec{Q}) = \frac{1}{\pi} f(\vec{Q}).
\]

Using the description of Equation 3.15, a function relating the Lorentzian form for frequency using the FWHM \(\Delta \nu(\vec{Q})\) can be derived, but this form will yield a slightly incorrect form that diverges from the solution by a factor of 2. This discrepancy was corrected in other works [10]. Thus, the definition
of the dynamic structure factor in Equations 3.12 and 3.14 is of the correct format. Once the dynamic structure factor has been obtained, this model can be applied directly to the incoherent dynamic structure factor obtained from experiment. In a single crystal sample, it is important to classify the expected directions along which hydrogen should diffuse within the PdH\(_x\), as was done by Sköld and Nelin [40]. Since bulk palladium is an FCC Bravais lattice, and it is expected for hydrogen to be found at octahedral interstitial sites which form an FCC sublattice with the same lattice dimensions as Pd, the expected HWHM as a function of \(\vec{Q}\) can be characterized with a single function [40]:

\[
\Delta \omega(\vec{Q}) = \frac{1}{3\tau_{\text{res}}} \left\{ 3 - \cos(\frac{L}{2}Q_x) \cos(\frac{L}{2}Q_y) - \cos(\frac{L}{2}Q_z) \cos(\frac{L}{2}Q_y) - \cos(\frac{L}{2}Q_y) \cos(\frac{L}{2}Q_z) \right\},
\]

(3.16)

where \(L\) is an important variable providing the magnitude of the jump length between the octahedral sites. In the case of an octahedral-octahedral jump, this distance is equivalent to \(\sqrt{2}a\), where \(a\) is the lattice parameter. For Pd, this implies that \(L\) is equal to 2.75 Å. Though the formulation in Equation 3.16 has proved useful in the single crystal case, it is prudent to create a more applicable description of the QENS broadening widths by taking a solid angle average of Equation 3.9:

\[
\frac{1}{4\pi} \int \int \Delta \omega(\vec{Q}) d\Omega = \frac{1}{4\pi \tau_{\text{res}}} \int_0^{2\pi} d\phi \int_0^\pi d\theta \sin \theta \left[ 1 - \exp(-iQL \cos \theta) \right]
\]

\[
= -\frac{1}{2\tau_{\text{res}}} \left[ -\cos \theta \int_0^\pi d\theta \exp(-iQL \cos \theta) \right]
\]

\[
= \frac{1}{2\tau_{\text{res}}} \left[ 2 - \int_{-iQL}^{iQL} \exp \frac{u}{iQL} du \right]
\]

\[
= \frac{1}{2\tau_{\text{res}}} \left[ 2 - \exp \frac{iQL}{iQL} \right]
\]

\[
= \frac{1}{2\tau_{\text{res}}} \left[ 2 - \exp (iQL) - \exp (-iQL) \right]
\]

\[
= \frac{1}{2\tau_{\text{res}}} \left[ 2 - 2i \sin(QL) \right]
\]

\[
\therefore \frac{1}{4\pi} \int \int \Delta \omega(\vec{Q}) d\Omega = \frac{1}{\tau_{\text{res}}} \left( 1 - \frac{\sin(QL)}{QL} \right),
\]

(3.17)

It is important to note that the extremal values of this function can be classified using the function \(\tan(QL) = QL\), implying that the first maximum in \(Q\) will occur at \(Q=1.634 \, \text{1/Å}\) if the previously given value for \(L\) is applied.

Once characteristic widths have been obtained for each measured \(Q\) value, it
is possible to create a fit of the data to Equation 3.17 that will allow for the simultaneous determination of $\tau_{res}$ and $L$, if $L$ were to be made a free parameter. It is then possible to obtain an experimental value for the diffusion coefficient using Einstein’s relation:

$$D = \frac{L^2}{6\tau_{res}} \quad (3.18)$$

In this case, the Einstein relation assuming three dimensional Brownian motion is adopted due to the polycrystalline average. As discussed in Chapter 2 when a series of diffusion coefficients is collected for a single system at different temperatures, it is possible to create a descriptive fit to the data using the Arrhenius relationship of Equation 2.2. This will relate the absolute diffusion coefficient $D_0$ and the activation energy $E_a$ for the diffusive process, which are both directly tied to the structural composition of the metal lattice as well as the dominant isotopic species of hydrogen utilized [43]. This full process has been applied in the aforementioned works to determine the bulk PdH$_x$ properties, and was more recently applied to determine the diffusivity of hydrogen with dislocations using fitting software to determine the characteristic FWHM values from $S_{inc}(\vec{Q}, E)$ data on the BASIS instrument [12]. Although the incoherent dynamic structure factor presented in Equation 3.12 classifies the expected QENS peak broadening, this is not by any means the only contributing aspect of the experimentally derived $S_{inc}(\vec{Q}, E)$. In fact, the full incoherent dynamic structure takes the form [12]:

$$S_{inc}(\vec{Q}, \omega) = \exp(h\omega/2kT)\left( \exp(-2W)(A_0(\vec{Q})\delta(\omega) + \sum_{i} A_i(\vec{Q})L_i(\vec{Q}, \omega)) \otimes R(\vec{Q}, \omega) + B(\vec{Q}, \omega) \right), \quad (3.19)$$

where $\exp(h\omega/2kT)$ gives the detailed balance factor, $\exp(-2W)$ is the attenuation due to the Debye-Waller factor, and $A_0(\vec{Q})\delta(\omega)$ is the elastic peak intensity. As the function relates, the major contributions to the experimental $S_{inc}(\vec{Q}, \omega)$ are described via a sum of Lorentzians that has been convoluted with the resolution function of the instrument, then added to a background term $B(\vec{Q}, \omega)$. The fitting software utilized performed the convolution of the resolution function with the QENS broadening, subsequently considering the addition of a uniform background term. Due to finite restrictions on the energy transfer for each instrument, wider Lorentzians were seen to be folded into the background term and narrow terms sometimes fell within the characteristic FWHM of the instrumental resolution. Considerations towards the Debye-Waller factor for the BASIS data has been presented elsewhere [88]. Through the process developed here, basic calculations of the diffusivity for hydrogen in metals was carried out for many bulk systems. However, as it has been determined that other considerations must be made to properly describe deformed PdH$_x$ dynam-
ics using $S_{mic}(\hat{Q}, \omega)$ [89], the following sections will detail the theorized diffusive process for the deformed system and how this will modify the expected structure factor and ISF.

\section{Theoretical Considerations for Material Processes in Deformed PdH$_x$}

\subsection{Dislocation Stresses and Solute Segregation}

In order to understand the complex process of diffusion within a dislocation network, it is important to briefly review the expansion made by Peierls-Nabarro [46, 47] upon Volterra’s postulated theory of dislocation structure. Volterra’s construction was made assuming that crystal planes would undergo a continuous displacement. However, applying the Burger’s vector description for a real crystal with a single edge dislocation showed that Volterra’s model assumed an aphysical discontinuity for the energy within the postulated dislocation core. In order to accommodate this new construction, Peierls-Nabarro established a model describing the one dimensional separation between top and bottom half planes as $\frac{b}{2}$, or half of the Burger’s vector magnitude. A depiction of this model has previously been presented in Figure 2.7. A full description of the derivation is provided by Hirth [44], so it will suffice to describe here the important results of the derivation. Peierls-Nabarro found that by assuming restoring stresses could be modeled with a sinusoid, a function describing the displacement along the crystal plane direction from the inserted half plane to the bottom plane could be given as

$$u_x = -\frac{b}{2\pi} \tan^{-1} \frac{x}{\zeta}, \zeta = \frac{d}{2(1-\nu)}$$

(3.20)

for an edge dislocation, where $\nu$ is Poisson’s ratio and $d$ is the spacing between crystal planes. This formulation led to a description for the width of a dislocation reliant solely upon the material properties, namely $2\zeta$. The Peierls-Nabarro description provided a good approximation to the atomic positions near a dislocation core, and also removed the artificial nature of the divergent energy function close to the core. An elastic energy calculation for atomic positions distant from the dislocation was found to be similar to Volterra’s calculation, but the Peierls-Nabarro model also accounted for a misfit energy due to the local stress induced on the stretched bonds due to the displaced half plane concept. Thus, the energy function is composed of a long-range elastic term that decreases as the core width increases and a localized misfit term that has a direct relationship to core width. The function can be written as
\[ E_{\text{total}} = E_{\text{elastic}} + E_{\text{surf. stress}} + E_{\text{misfit}} \]

\[ = \frac{G b^2}{4 \pi (1 - \nu)} \ln \frac{r}{2 \zeta} + \frac{G b^2}{4 \pi (1 - \nu)} \left( \frac{1 - 2\nu}{4(1 - \nu)} \right) + \frac{G b^2}{4 \pi (1 - \nu)} \]  

(3.21)

where \( G \) is the shear modulus and \( \zeta \) is found in Equation 3.20. Here, an additional consideration has been given to the stress incurred in the near-core region, termed the “surface stress” energy because its origin can be considered as the work of an additional restoring force around a cylinder containing the dislocation core structure. Criticisms of this representation have been complied by Hirth [44] on the basis of a continuous elastic approach to a discrete model, the use of a sinusoidal potential in light of true interatomic forces, the assumption of linear elasticity in the core, and the ignorance of temperature effects. Regardless of these concerns, it is well known that the stresses inherent to a dislocation structure will assume a known form that directly affects how a dislocation will interact with interstitial H atoms. The hydrostatic stress around an edge dislocation can be derived as [44]:

\[ \sigma_H = \frac{G b (1 + \nu)}{3 \pi (1 - \nu) \frac{\sin \theta}{r}} \]  

(3.22)

This formulation can be qualitatively visualized as is done in Figure 3.1. Based upon the stated equation, the material will experience a compressive stress immediately below the dislocation glide plane with an origin at the core, while a region of expansion will exist above the glide plane to counteract the compressive stress. The implications of this stress regime in terms of interaction with solute atoms was investigated by Cottrell and Bilby [49] shortly after the Peierls-Nabarro model was developed. It was hypothesized that due to the compressive stress gradient, solute atoms would populate sites close to the dislocation core, forming what would be termed as a “Cottrell atmosphere” in the surrounding region. Although significant consideration has been given to mobile dislocations and their interactions with Cottrell atmospheres [44], the system under study will not see external stress applied and should thus avoid this additional complication. The structure of dislocations acting as a segregating force for H interstitials has been probed extensively via SANS measurements, as discussed in Chapter 2. In these measurements, it was common to choose a hydrogen concentration large enough to fully saturate the rod-like dislocation structures, allowing for a clearer picture of the effects due to elastic stress upon interstitial H atoms.

In the context of SANS, the Fermi-Dirac equation (presented as Equation 2.3) is generally utilized to describe the concentration of hydrogen in the dislocation elastic stress field. A further elaboration of the implications of this distribution was composed by Al-Nahlawi and Heuser [50], where the Fermi-
(a) Qualitative representation of stress field near an edge dislocation [44].

(b) Region of attractive hydrostatic stress below the glide plane (dashed line). Circles represent the stress equation calculated at radii R away from the base of the dislocation [60].

Figure 3.1: From the surrounding stress fields, it can be envisioned that solute H atoms would be attracted to the compressive region immediately below the inserted half plane, while a repulsion behavior is expected above the half plane. This representation models behavior distant from the core structure.

Dirac distribution was integrated over in order to determine the number of hydrogen atoms contained per unit length of dislocation. The expected core concentration was also calculated, assuming a constant binding energy within the core and a lack of H-H bonding interaction, to be:

$$\left( \frac{N}{L} \right)_{\text{core}} = \frac{\gamma}{b} \frac{1}{1 + \eta \exp \left( \frac{-E_b}{k_B T} \right)}$$  \hspace{1cm} (3.23)

where $\eta$ represents the ratio $\frac{1-C_0}{C_0}$ of the bulk concentration $C_0$ and $E_b$ is the core binding energy. This relationship implies that interstitial sites exist at intervals of a Burger’s vector within the dislocation core, while the ratio $\frac{\gamma}{b}$ provides a scaling factor for the actual number of H interstitials per unit dislocation length. The relationship also relates that an increase in temperature will result in a decrease of the hydrogen concentration within the core region, a result that was seen later by other studies. This concept was then applied in order to numerically determine the expected hydrogen concentration within the Cottrell atmosphere. A further argument [57] extended upon this line of logic, using a balance of the chemical potential within the elastic and core regions to express $[H]$ and the expected radius of hydrogen found around the dislocation. Further models were developed [70] to computationally model the effects of H-H interaction, the anharmonic Pd potential, and strain fields in core/near-core regions upon the expected temperature and bulk concentration dependence of the $[H]$ field near the dislocation. Through these results, a depopulation temperature near 300K was determined for low concentrations of hydrogen, as was previously discussed. Although SANS studies allowed for thorough investigations of the elastic stress region and gave insight into the concentration found within the
core, the use of $[\text{H}]/[\text{Pd}] \sim 0.1$ did not allow for insight into the intrinsic diffusion processes within the fully saturated core region. Theories have been proposed as to how hydrogen will interact with the core region, with many experimental results pointing towards enhanced diffusion within the dislocation core structure as detailed in Chapter 2. The base of interstitial diffusion study within the dislocation core structure is due to Love [48], who postulated the existence of dislocation pipe diffusion. A detailed look into the diffusion process followed by hydrogen in deformed metals will incorporate this consideration, and will be presented in the next section.

3.2.2 Models for H Diffusivity within Deformed Metals

The first detailed model for hydrogen diffusion within a deformed metal medium is due to a set of works by Kirchheim et al. [58, 57, 79, 80, 81] that developed a theory in the context of experimental results using electrochemical methods to gauge the diffusive mechanism. A qualitative discussion has already been presented, but a brief quantitative explanation of the theory is still desirable. A model employing the chemical potential and heat of hydride formation within a dislocation upon a Fermi-Dirac distribution was first created. This logical step determined that at certain concentrations, the experimental chemical potential would identically match the theoretical Fermi energy of the system. This concept was elaborated upon by saying the site density of available trap sites for H interstitials within the dislocation could be described using a Gaussian distribution function:

$$n(G) = \frac{dN}{dG} = \frac{1}{\sigma \sqrt{\pi}} \exp \left[ - \left( \frac{G - G^0}{\sigma} \right)^2 \right], \quad (3.24)$$

where the number of sites at a certain energy $G$ is envisioned as a distribution of width $\sigma$ around a reference state $G^0$. A physical manifestation of this concept can be seen in Figure 3.2 which relates how the setup assumes a range of trap energies but that saddle points between the traps are assumed to have a constant reference energy. This configuration of the trap sites allowed for the description of hydrogen diffusion within a deformed Pd lattice as per further work [80].

In this work, Kirchheim begins by assuming that a form of the Fermi-Dirac distribution can be used to describe the relationship between the concentration of hydrogen within certain trapping sites ($C_i$) and the concentration of trapping sites of a given energy state ($C^0_i$). Integrating across this distribution with respect to the density of sites from Equation 3.24 determines $c_H$, the total hydrogen concentration:

$$c_H = \int_{-\infty}^{\infty} \frac{n(G_i) dG_i}{1 + \exp \left( \frac{G_i - \mu}{RT} \right)}, \quad (3.25)$$
which directly provides the relationship between the chemical potential of hydrogen $\mu$ and the total concentration. However, in developing the methodology for describing the H diffusion within a deformed system, Kirchheim relaxes the Fermi-Dirac equation description and opts to use a step function approximation in order to describe the chemical potential. This leads to the determination of the chemical potential as:

$$
\mu = G^0 + \text{erf}^{-1}(1 - 2c_H).
$$

He then separately derives an equation for the net hydrogen flux within a deformed metal for a cubic crystal:

$$
J = -\frac{1}{6} \frac{\partial c_H}{\partial x} L^2 \int \int \Gamma_{i0} \exp\left(-\frac{G_{ik}}{RT}\right) \frac{\partial}{\partial c_H} \frac{n(G_i)}{1 + y_i} \frac{n(G_k)}{1 + y_k} \exp\left(-\frac{\mu - \bar{G}}{RT}\right),
$$

where the net flux $J$ is a function of the absolute jump frequency $\Gamma_{i0}$ that occurs across two distributions of trap sites with energies $G_i$ and $G_k$. In the case of a continuous spectrum of sites energies, this model yields an equation for the effective diffusivity within a deformed sample:

$$
D_{ef} = D \frac{\partial}{\partial c_H} (1 - c_H)^2 \exp\left(\frac{\mu - \bar{G}}{RT}\right),
$$
where \( \tilde{G} \) gives the site energy for an undeformed material and the chemical potential can be determined either experimentally or theoretically. This formulation can be further refined by including a calculated level for \( \tilde{G} \) and including the chemical potential of Equation 3.26 \[80\]:

\[
D_{ef} = D_0 \sigma \sqrt{\frac{\pi}{RT}} \exp \left( \text{erf}^{-1}|2C - 1| \right)^2 \exp \left( \frac{\sigma \text{erf}^{-1}|2C - 1|}{RT} \right),
\]

which explicitly defines the effective diffusion coefficient as a function of the dimensionless H concentration \( C = c_H/M \) (where \( M \) is the interstitial sites available per volume) and the standard deviation of the Gaussian trap site distribution. As discussed in Chapter 2, Equation 3.29 was successfully used to describe electrochemical diffusion results for a cold worked Pd sample within the concentration range of \( 10^2 \) to \( 10^4 \) at. ppm., and provided an explanation for the strong correlation between concentration and diffusivity within a deformed metal. In this case, the experimentally determined chemical potential was applied. However, divergence from the model at lower concentration could not be directly explained by this formulation, and were qualitatively described as being the result of enhanced diffusion along dislocations. It is also of note that the experimental specimens tested were cold worked but not cycled across the miscibility gap, leading to a less regular dislocation network than would be expected out of a cycled sample \[95\]. Kirchheim later considered the H-H interaction while performing analysis on a nanocrystalline PdH\(_x\) sample \[82\] using a simple modification to the assumed average energy.

Further advancements upon Kirchheim’s original theory were made by Brouwer et al. \[84\] and more recently by Gapontsev et al. \[83\]. As remarked upon by Gapontsev, the Brouwer model refines that of Kirchheim by incorporating five nearest neighbor configurations, accounting for the H-H interaction through an additional term in the Fermi-Dirac concentration formula, and regards site blocking of nearest neighbor interstitials by hydrogen atoms. This leads to a more complex formulation of Equation 3.28 which is presented in full by Gapontsev et al. \[83\]. Elaborating on this approach, the authors note that neither Kirchheim nor Brouwer have effectively taken into account the non-negligible effects of a hydrogen concentration gradient upon the chemical potential of the system, instead regarding the initial and final orientations for an H atom after a diffusion event as having the same \( \mu \). They proceed to use a linear dependence to relate the change in chemical potential, using the length of a diffusive jump for hydrogen \( L \) to create the function:

\[
\mu_2 = \mu_1 + \frac{d\mu}{dx}. \tag{3.30}
\]

This expression led the authors to create a general formalism for the net flux within a diffusive system, described as the method of configuration sums,
by considering the site occupation permitting diffusive jumps as a function of this chemical potential. The net flux formalism was then compared against Fick’s law of diffusion to obtain a general equation for the expected diffusion coefficient:

\[
D_{ef} = \frac{2AL}{\bar{\tau} \bar{z} M} \sum_{\chi, \chi'} f(\chi, \chi') \exp(-V(\chi, \chi')/kT)\nu_{\chi'}q_{\chi'}[\nu_{\chi'} + q_{\chi'}] \\
\sum_{\chi} f(\chi)\nu_{\chi}q_{\chi}, \tag{3.31}
\]

where the applied variables represent both the orientation of the local crystal structure and the local energy potential. It is assumed that thermal vibrations for interstitial H atoms can be described with an average period \( \bar{\tau} \) and that the probability a diffusive jump occurs between two distinct sites is approximately \( 1/\bar{z} \), where \( \bar{z} \) is the coordination number of the nearest neighbor interstitial sites between which such a jump could occur. As \( \nu_{\chi} \) relates the probability of H site occupation at position \( \chi \) while \( q_{\chi} = 1 - \nu_{\chi} \) relates the probability of site vacancy, Equation 3.31 relates the diffusion coefficient to the probability of site blocking as well as a general function for the atomic structure \( f(\chi, \chi') \) and the potential energy landscape \( V(\chi, \chi') \). It should be noted that the occupation term \( \nu_{\chi} \) also accounts for variability in saddle point energy \( \epsilon_{\chi} \). A physical explanation for how this general formulation for the energy potential would appear to an interstitial H atom is shown in Figure 3.3.

![Figure 3.3](image)

Figure 3.3: Visualization of revisions made by Gapontsev et al. to the potential energy landscape proposed by Kirchheim. This model permits a variable trap site energy function \( V(\chi, \chi') \) as well as a variable saddle point energy \( \epsilon_{\chi} \).

Gapontsev et al. then proceeded to derive a more specific formulation for the case of amorphous metal systems containing low concentrations of hydrogen, followed by a direct comparison to the results of Kirchheim. While the details of this derivation will not be fully divulged due to their extensive length and
can be found in the work [83], the important results will be expressed here. Classifying the distribution function for interstitial sites in a disordered system using $\alpha$, a term describing the local dilatation of amorphous interstitial sites as compared to a typical crystal structure, the distribution function for single interstices can be written as:

$$W(\alpha) = \frac{1}{\sqrt{2\pi p}} \exp\left(-\frac{\alpha^2}{2p}\right), \quad (3.32)$$

in which $p$ is a function derived from an experimentally determined radial distribution function $g(r)$ for an fcc lattice,

$$p = \frac{8\sigma_1^2 + \sigma_2^2}{a^2}, \quad (3.33)$$

where $\sigma_1$ and $\sigma_2$ are fitted HWHMs for the first two peaks in $g(r)$ and $a$ is the lattice parameter. In effect, using the function $p$ sought to improve upon the Gaussian distribution of trap sites by incorporating an experimentally determined measure for site deformation. A lengthy formulation considering the aforementioned variable trap and saddle point energies was given, then compared to Kirchheim’s model. Gapontsev et al. showed that by making the assumption of a constant saddle point energy while neglecting the correlation between atom type and lattice dilatation, their formulation yielded an effective diffusivity of:

$$D_{ef} = \frac{2AL}{\tau z c_{H_{\text{max}}}} \exp\left(-\beta(E_0 - \epsilon_0)/kT\right) \sqrt{1+2\delta p/kT(1-C)^2}, \quad (3.34)$$

which was analogous to the effective diffusion found in Equation 3.29. However, this formulation improved upon the assumption of a Gaussian distribution of trap sites with standard deviation $\sigma$ made by Kirchheim by instead assuming a Gaussian distribution of site dilatation (Equation 3.33), creating an experimentally motivated refinement of the site energy distribution given by Equation 3.24:

$$n(\epsilon) = \frac{1}{\sqrt{2p\delta \pi (\epsilon - \epsilon_0)}} \exp\left\{-\frac{\epsilon - \epsilon_0}{2p\delta}\right\}, \quad (3.35)$$

where $\delta$ is a free parameter describing the effect of local lattice dilatation upon the saddle point energy $\epsilon$. The general model presented by Gapontsev et al. can be considered as the most accurate analytical model for H diffusivity within a deformed lattice due to its use of nearly every parameter under consideration. Feasibly, the general formalism could be applied to a radial distribution function for the interstitial network within the core as determined computationally using DFT, as was done by Schiavone et al. [89], and then directly compared to the experimental results for very low [H] systems. This procedure will not be attempted here, due to the difficulty of relating this analytical formulation.
for diffusivity to QENS results. Instead, the next section will reflect upon the choice of a continuum description of the relaxation times for diffusion processes within a deformed Pd lattice.

3.3 Theory of QENS Analysis for Deformed $\alpha - \text{PdH}_x$ Systems

As was expounded upon in Chapter 3.1, due caution must be taken when describing deformed PdH$_x$ dynamics using $S_{\text{inc}}(\vec{Q},\omega)$ [89]. Previous consideration has been given to complex models describing the expected diffusivity for H interstitials in deformed metals. All of the discussed theories have attempted to further the understanding of different contributing factors to the distribution of available trap site energies and residence time within these trap sites. In the following formulation, the dynamics of H within a dislocation core will be considered in reference to results obtained from QENS. It should be recalled that in the construction of Equation 3.19 the elastic contributions and QENS broadening found via the experimental $S_{\text{inc}}(\vec{Q},\omega)$ will be convoluted with the instrumental resolution function. When considering this system in the energy domain, the amplitude of the QENS broadening with respect to that of the resolution function does not have a well-defined relationship, though for many systems the relationship between the QENS intensity and the elastic intensity is a known function. As noted by Bée [11], the intermediate scattering function is a clear indication of the elastic incoherent structure factor (EISF), namely the ratio between elastic and QENS intensities that is demarcated as $A_0(\vec{Q})$ in Equation 3.19. In the case of hydrogen in metals and other systems with dynamical disorder, Bée points out that the ISF should trend to zero, thus eliminating the elastic contribution. To avoid the concern of additional contributions due to elastic intensity that could occur if not properly accounted for, a low temperature sample is in general chosen as the instrumental resolution instead of a pure incoherent scatterer. Although the elastic contribution is not a concern for the system, the fitting method adopted originally was dependent on proper scaling of the resolution function as compared to the QENS broadening during the convolution process. Additionally, when considering QENS broadening from multiple instruments, it is not possible to simultaneously analyze the entire probed range of energies due to overlap between the instrumental resolution and maximum energy transfer. As was explicitly seen during the $S_{\text{inc}}(\vec{Q},\omega)$ analysis of the QENS data from BASIS, the QENS broadening attributed to DPD was difficult to determine at temperatures near the hydrogen detrapping limit because the FWHM of the Lorentzian was on the order of the energy transfer window and led to its inclusion into the background term. Similarly, slower processes were folded into the resolution function’s range on CNCS and act similarly to an elastic intensity [11]. In consideration of this difficulty with the
dynamic structure factor, an interesting and useful relationship that exists for the intermediate scattering function can be exploited in order to remedy these concerns [36]:

\[ S_{\exp}(\vec{Q},\omega) \simeq S_{\text{inc}}(\vec{Q},\omega) \boxtimes R(\vec{Q},\omega) \overset{\text{FT}}{\longrightarrow} I_{\exp}(\vec{Q},t) \simeq F_{\text{inc}}(\vec{Q},t) \ast R(\vec{Q},t). \]

(3.36)

Equation 3.36 relates simply the difference between mathematics for the dynamic structure factor \( S(\vec{Q},\omega) \) and the intermediate scattering function \( F(\vec{Q},t) \). Theoretically, it is possible to define the resolution function \( R(\vec{Q},\omega) \) as the instrumental resolution obtained from regarding the Q dependent low temperature data as a function with a symmetric energy transfer window. The resolution function in the time domain \( R(\vec{Q},t) \) is determined by taking the Fourier transform with respect to time of either a set of Gaussians fit to the resolution curve for each Q bin, or by taking the FT of the instrumental resolution function \( R(\vec{Q},\omega) \) directly. Doing the same transformation for \( S_{\text{inc}}(\vec{Q},\omega) \) then leads to \( F_{\text{inc}}(\vec{Q},t) \) through a simple division process. As long as the \( S_{\text{inc}}(\vec{Q},\omega) \) does not include a uniform background, the ISF will trend to 1 at \( t=0 \). However, for any dynamic structure factor that includes a uniform background, the Fourier transformation will cause the background to manifest itself as a delta function at \( t=0 \) [11], with an intensity equivalent to the strength of the background contributions. In the situation at hand, the wide energy transfer window for CNCS leads to discernible values for low time scales (less than .5 ps in the case of higher Q bins), but a divergence from \( F_{\text{inc}}(\vec{Q},0)=1 \) will still occur in the case of deformed PdH\(_x\). Equation 3.10 has previously defined the expected exponential behavior of the ISF for the Chudley-Elliot model, in which the exponential is defined by a single decay process. This allows for comparison to the Chudley-Elliot model for bulk annealed PdH\(_x\), where a diffusivity can be procured from the range of Q-dependent \( \tau \) values obtained for each temperature. Within the context of the Fourier transformation process, a few key equations were necessary in order to modify the discrete data sets used. The first such equation incorporates the inversion of the domain during the Fourier transform as well as the shift from angular frequency to linear frequency, resulting in an explicit function of time. As the \( S_{\text{inc}}(\vec{Q},\omega) \) is experimentally determined as a function of energy, a conversion factor is necessary to relate the energy domain and the time domain required for \( F(\vec{Q},t) \), namely

\[ f(E)(\text{meV}) \overset{\text{FT}}{\longrightarrow} \left( \frac{2\pi}{f(E)} \right) \left( \text{rad} \right) \ast \text{factor} = f(t)(\text{ps}), \]

\[ f(t)(\text{ps}) = \frac{\hbar}{f(E)} \frac{(\text{meV})/(\text{ps})}{\text{meV}} \rightarrow \text{factor} = \frac{\hbar}{2\pi} \frac{(\text{meV} - \text{ps})}{(\text{rad})}, \]

(3.37)
which shows that the discrete points within the inverted energy domain \( \frac{2\pi}{f(E)} \) must be multiplied by a factor of 
\( \frac{\hbar (eV-s)(rad)}{10^{12}ps/1sec} \times \frac{10^3 meV}{eV} = 0.6582 \frac{(meV-ps)(rad)}{sec} \)
in order to determine discrete points for the time domain \( f(t) \). This equation can be used to determine the valid range of data within the time domain. As discussed by Schiavone et al. [89], the range of useful data in the energy domain will be limited by the energy transfer window. Because the instrumental resolution is variable in Q, the conversion mentioned in Equation 3.37 provides a simple relationship that translates the energy transfer window to a Q-dependent time regime, as will be touched upon in Chapter 4.

In order to classify the intermediate scattering function with regards to the aforementioned descriptions for H diffusion within deformed Pd, a modification of the single exponential form will be adopted. This modification will be made to acknowledge the theories of Kirchheim and Gapontsev, which rely upon classification of the trap site energies using various continuum models. These previous theoretical considerations have discussed the relationship between concentration and diffusivity, but as noted do not account for the possibility of enhanced diffusion along dislocations at sufficiently low [H]. The ab initio studies performed by Trinkle and Schiavone for a single hydrogen [12, 89] point to the existence of dampened diffusion barriers in the expansion region below the inserted half-plane, as well as a distinct diffusion pathway within the core region with lowered diffusion barriers. They postulate that for sufficiently low concentrations, dampened core barriers allow hydrogen atoms move from the lowest energy states below the partial core to the slightly higher energy states inside the partial cores, allowing for diffusive jumps within the core region that bypass filled trap sites. In order to classify this pathway correctly, the effects of hydrostatic stress due to a Cottrell atmosphere near the core must be acknowledged. It can be postulated that as [H] near the core increases, the expected Fermi-Dirac distribution will lead to a similar distribution of residence times within the near-core region, as the introduced stresses will relax the diffusion barriers between the remaining open sites. Following these lines of logic, two distinct diffusive mechanisms could serve as contributions to the intermediate scattering function:

1) Enhanced dislocation pipe diffusion within the core due to the inherent deformation of the dislocation geometry, which will be a function of both concentration and temperature. As concentration increases but remains below a critical level, the induced lattice strain from additional hydrogen atoms below the core will relax the diffusion barriers into the core region and permit more frequent jumps within the core itself. However, past a critical level the increased trapping within the sites below the inserted half plane will lead to a site-blocking mechanism, decreasing the contribution of inner core diffusivity. This concentration increase also will increase the activation energy within the core, because the entropy of configuration will increase as trap sites are filled. In the context of temperature, larger temperatures near the detrapping temperature will en-
courage higher sampling of jumps in the near-core and bulk region as the trap sites are vacated.

2) Diffusion within the near-core region will occur at temperatures near the detrapping temperature, as full trapping will only occur when the atoms are thermally confined to these lower energy states. Due to the classification of the concentration with a Fermi-Dirac distribution and considering the effects of hydrostatic stress from each H, the diffusion within the near-core region can be considered as a series of jumps following a continuum of site residence times. As the concentration is increased, the filling of trap sites will lead to a nearly uniform stress distribution. Once these sites are filled, the bulk activation energy will be observed. However, it is expected that temperatures near the detrapping temperature will also encourage diffusivity within bulk Pd, with an increase in the contribution of this process above the detrapping temperature. Thus, for sufficiently low concentrations, contributions to the intermediate scattering function for diffusive processes occurring within the near-core region and bulk region can be expected, with a relatively larger contribution from the bulk region occurring above the detrapping temperature of 300K.

For the proposed theory contained herein, it will be assumed that the concentration tested is sufficient for enhanced diffusivity within the core. It is expected that hydrogen atoms will populate trap sites below the core randomly, and thus a range of possible residence times can be classified. The diffusive process within the confined dislocation region will be classified using a continuum description that has previously been adopted to describe dynamics of water contained to a molecular sieve [91]. The model assumes that the sieve confines the movement of water to a single translational direction, not unlike the assumed pathway for inner core dislocation pipe diffusion. Diallo uses a similar model to describe the intermediate scattering function obtained from QENS for water diffusion in porous carbon microfibers, including a consideration for the elastic contribution that will not be needed here [96]. The base formulation of this model is the stretched exponential, also known as the Kohlrausch-Williams-Wattts (KWW) function in tribute to Williams and Watt, who first used it to describe the dielectric spectra of the polymer polyethyl acrylate [97]. In the context of the ISF, the stretched exponential takes the form:

$$F_{inc}(Q,t) = F_0 \exp\left(-\left(\frac{t}{\tau_{KWW}}\right)^{\beta_{KWW}}\right),$$

(3.38)

where \(\beta_{KWW}\) is the stretching parameter and \(\tau_{KWW}\) is the relaxation time of the stretched exponential. The stretching parameter has a range of \(0 < \beta_{KWW} < 1\), and \(F_0\) can vary as a result of background contributions. If elastic contributions are considered, an additional \((1 - F_0)\) term is added to the stretched exponential to account for the existence of time independent processes that lead to a nonzero decay in the ISF as \(t \rightarrow \infty\). It can be seen that if \(\beta_{KWW} = 1\), then the usual exponential form describing a single jump process is obtained. Thus, \(\beta_{KWW}\)
can be said to define the level of heterogeneity within the system, and will vary as a function of momentum transfer and temperature \[36\]. The stretched exponential can be further analyzed using the average relaxation time within the system \(\langle \tau \rangle\) by integrating across the entire time range \[96\]:

\[
\langle \tau \rangle = \int_0^\infty \left( \frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \frac{1}{\beta_{KWW}} \Gamma \left( \frac{1}{\beta_{KWW}} \right), \quad (3.39)
\]

where \(\Gamma(x)\) is simply the gamma function. Thus, at a given temperature, the diffusive process within the core region of a dislocation can be classified using two parameters, \(\langle \tau \rangle\) and \(\beta_{KWW}\). This method avoids the complication of using a discrete jump matrix within the dislocation geometry while still providing representative trends about the nature of the diffusive process. There exists both an analytical approximation as well as numerical methods for transforming the stretched exponential into the energy domain \[95\], a method that could be considered more accurate since the fit would be performed with known values for the instrumental error at each energy bin. However, due to the desire to analyze different instruments simultaneously using the intermediate scattering function, this method was not directly applied. From the analysis of BASIS results in the energy domain, it was seen that the more rapid diffusion processes were at times diluted by the uniform background term due to the constraints of the energy transfer window \[12\]. With this knowledge and the expectation that the bulk diffusion contribution to the ISF will occur across a distinct time range from that of the dislocation enhanced diffusion,

\[
F_{inc}(Q,t) = F_0 \exp \left( - \left( \frac{t}{\tau_{KWW}} \right)^{\beta_{KWW}} \right) + (1 - F_0) \exp \left( - \frac{t}{\tau} \right), \quad (3.40)
\]

where the stretched exponential classifies DPD and the single exponential refers to the homogenous bulk diffusion jumps. A known property of the Fourier transform is that addition in the original domain corresponds to addition in the transformed domain. Thus, instead of using a discrete sum of Lorentzians to describe the diffusive jumps, the dynamic structure factor could be written as a sum of the Fourier transformed stretched exponential and a single Lorentzian, convoluted with the instrumental resolution. A feasible process to be followed for the proper application of Equation 3.41 is to truncate the data such that the behavior of only one of the terms in captured, then use the gathered fitting parameters to characterize the whole data set. It should be noted that \(\langle \tau \rangle\) is analogous to an averaged HWHM in the energy domain for a specific Q value, and that this \(\tau\) value does not define the residence time \(\tau_{res}\). It will be difficult to ascertain information about the diffusion coefficient from the stretched exponential data, since a relationship to the mean relaxation time \(\langle \tau \rangle\) is not defined for an amorphous metal. However, it is likely that a comparison
could be made between the discrete sum of weighted Lorentzians described by Schiavone et al. [89] and the mean relaxation time. Also, in the case of constrained water molecules, Swenson et al. proposed the use of the Gaussian jump length distribution model:

\[
\frac{1}{\langle \tau \rangle} = \frac{1}{\tau_{\text{res}}}[1 - \exp(-Q^2L^2/6)],
\]

(3.41)

which is a typical representation of the Q-dependent function describing the translational jump diffusion process. Thus, a comparison of the mean relaxation time to the residence time is possible as long as a model exists relating HWHM to Q. It is conceivable that with the two central parameters gained from the stretched exponential term and the relaxation time from the single exponential term, the intermediate scattering function \( F_{\text{inc}}(Q,t) \) will characterize the entire range of diffusive processes occurring at a certain temperature, and will also yield the ratio of core/near-core diffusion processes to those of the bulk crystal in the context of the H detrapping temperature.
Chapter 4

Experimental and Analytical Methods

4.1 Neutron Scattering Instrumentation

In order to test the feasibility of a multiple instrument approach to analyzing QENS data, a set of analyses were performed at the Spallation Neutron Source at Oak Ridge National Laboratory as well as the High Flux Backscattering Spectrometer (HFBS) at NIST. The initial tests were performed on the first set of samples described below, utilizing the Backscattering Silicon Spectrometer (BASIS) facility at SNS. Similar to other backscattering instruments, both HFBS and BASIS use the indirect geometry orientation, implying that the determination of the neutron energy transferred to the sample $\Delta E = E_i - E_f$ relies upon a band of incident neutron energies $E_i$ and a fixed final energy $E_f$.

On BASIS, this final energy is dictated by the backscattering of neutrons from Si(111) analyzer crystals upon a linear set of position-sensitive He-3 detectors [99]. At the time of this measurement, 18 Si(111) crystal panels were in use, allowing backscattering across $150^\circ$ horizontally and around $22^\circ$ perpendicular to the instrument plane, creating the ability to probe about 2 steradians or about 16 percent of the $4\pi$ solid angle. The backscattered neutron events are then captured by two arrays of 56 He-3 neutron detectors set within the backscattering window. Unlike these backscattering spectrometers, the other instrument employed has a direct geometry orientation, implying that $E_f$ is allowed to vary and $E_i$ is within a narrow range of energies. Instead of a near-linear target of He-3 detectors, the Cold Neutron Chopper Spectrometer (CNCS) utilizes an arced array of 400 He-3 detectors covering a range of $-50^\circ$ to $+135^\circ$ in the plane of scattering and approximately $\pm 16^\circ$ perpendicular to this plane, subtending about 1.7 steradians of the solid angle [100]. Schematics for the orientation of these two instruments can be found in the Appendix as Figures A.1 and A.2. These spectrometers differ in their method of determining spatial dependence, as is shown in Figure 4.1 as the direct geometry instrument will determine $\vec{Q}$ as the resultant of $\vec{k}_f - \vec{k}_i$ directly whereas the indirect geometry instrument will ascertain $\vec{Q}$ once the scattered neutron has been reflected.

In general, the spatial information gained will be coarsened via a binning process in an attempt to dissuade spurious contributions to the dynamic structure factor from certain detectors. Although their methods of spatial differentiation
are incongruous, direct and indirect (backscattering) instruments on a spallation neutron source both use the time-of-flight (TOF) property to obtain the scattering system’s energy transfer $\Delta E$. The TOF method can be summarized by saying that the time over which a neutron covers a characteristic length within the instrument determines the change in velocity from before scattering to after the event occurs, which can then be interpreted as a change in energy. The TOF method on a direct geometry instrument such as CNCS can be acknowledged by assuming that the instrument design is as shown in Figure A.2. CNCS uses a 300 Hz Fermi chopper and a 300 Hz double-disk chopper to shape the incident neutron beam and then generate the small $\Delta E_i$ required of direct geometry instruments [100]. A set of 60 Hz disk choppers is also employed to avoid “frame overlap” of the neutron pulses, ensuring that higher energy neutrons from each pulse do not interact with lower energy neutrons from previous pulses. A simple equation can be used to estimate how the incident neutron flight time is found,

$$t = \frac{\lambda m_n L}{h},$$  \hspace{1cm} (4.1)$$

where $t$ is the flight time of the neutron, $L$ is the distance between the primary choppers, $\lambda$ gives the neutron wavelength, $m_n$ is the mass of the neutron and $h$ is Planck’s constant. Once the neutron beam has impinged upon the sample, the scattered neutrons are collected by the detector array, which permits accounting of each neutron as a temporal event at a specific detector. The indirect geometry orientation at BASIS also employs the TOF method, but does so slightly differently. Instead of creating a narrow incident energy band as on
CNCS, a series of three choppers is generally operated at 60 Hz with different allowance angles on each, with the goal of transmitting a neutron bandwidth of \( \sim 0.5 \text{ Å} \) centered near the Si(111) elastic reflection wavelength of 6.267 Å in order to include the elastic line into the permitted Bragg reflection from the silicon wafers back towards the detector array [99]. It is important to note that since the spallation source is used, the implementation of BASIS differs from a reactor-based backscattering spectrometer in regards to geometry and energy transfer capabilities. On a reactor driven system, either a monochromator or neutron choppers can be applied in order to obtain a consistent \( E_i \) within the system. On the SNS beamlines, detectors can be positioned outside of the sample plane, which allows for the instrument’s analyzer crystals and detector sets to rest both above and below the incident neutron beam, as is seen in Figure A.1.

The discussed geometries of the two basic neutron scattering analysis methods have benefits to the experimenter by creating a variety of distinct useful conditions under which samples can be tested. A reactor driven backscattering spectrometer would allow for an energy transfer \( \Delta E \) range of only 30-40 \( \mu \text{eV} \), implying that events outside of this range would be manifested as a uniform background component. On BASIS however, the use of the silicon crystals and the offset detector banks allows for an energy transfer range of about \( \pm 170 \mu \text{eV} \), which is also complemented by the use of backscattering geometry. Due to the use of near perfect silicon crystals, an energy resolution with a FWHM of around 3.4 \( \mu \text{eV} \) for a vanadium test sample was obtained, representative of the instrument resolution due to vanadium’s small coherent scattering length [99]. For the BASIS studies in question, the gathered data was sorted into 9 spatial Q bins, and the resultant energy transfer window captured for the QENS broadening is about \([3.4,100]\) \( \mu \text{eV} \). Converting from an energy transfer window to the time domain using Equation 3.37, this translates to an operational time range of \([41.33, 1215.8]\) ps. Thus, the range of usable energies allows the instrument to accurately probe relaxation times on the order of several hundred ps, the range in which QENS broadening due to bulk diffusive within PdH\(_x\) was expected to occur. Unfortunately, the fitting procedure used to model the QENS broadening within the energy transfer window of BASIS made it difficult to quantitatively describe the BASIS data using multiple Lorentzians, especially the broad Lorenztian component. This difficulty was also encountered in some regards in the recent analysis performed by Kofu et al. [93]. This was due to competition between the curves with larger characteristic FWHMs and the uniform background component. This inability to resolve the BASIS data to its fullest extent was one of the motivations behind performing comparable tests on an instrument with a larger energy transfer window, assuming that this would create a better picture of the diffusion process within dislocations. The CNCS instrument operates over a wider dynamic range than BASIS, at the cost of a less defined energy resolution. The instrument can operate in two modes, high
resolution or high flux (HR and HF respectively), which are produced via small modifications of operating parameters such as chopper speed and slit width in order to change the effective energy transfer range of CNCS. The HF mode has a poorer instrumental resolution on a vanadium sample than the HR mode (59 µeV versus 42 µeV), but also is capable of greater neutron flux incident upon the sample (7.6*10^5 n/sec MW versus 2.6*10^5 n/sec MW), allowing for lower sampling times in order to obtain sufficient counting statistics for the scattering data [100]. For this set of tests, the CNCS HR configuration was utilized, with E_i=3 meV yielding 180-230 counts per second in preliminary tests of the scattering system. The obtained BASIS data resides within a symmetric energy transfer window of ±110µ eV, the CNCS energy transfer window range of [-10, 2.8] meV is much more extensive. In this context, positive and negative quantities of energy transfer reflect the possibility for neutrons to either lose or gain energy upon scattering. While the implications of these upscattering or downscattering mechanisms will be further discussed in Section [4.4], it will suffice to point out here that the expected maximum energy range of [42 µeV, ~ 10 meV] translates to an operational time range of [~ .41337, 98.42] ps. Including CNCS into the deformed PdH_x will thus allow for the more rapid diffusivities to be captured, and due to the overlap between the measured time scales will allow for simultaneous analysis of the data from both instruments as long as the samples tested have comparable dynamics. It should be noted that due to the limitations on resolution for CNCS, it will be difficult to properly describe the annealed diffusive process at room temperature as the characteristic Lorentzian curves would have a width less than that of the instrumental resolution, leading to these terms being folded into the elastic contribution term when performing fits to the data. At higher temperatures, this would not be the case, and CNCS could also be of use in the annealed system analysis.

4.2 Sample Preparation

A set of precise techniques developed for creating low concentration metal hydrides were used in the creation of the samples under analysis on the QENS instruments discussed. In the case of the materials created for BASIS and HFBS analysis, palladium with 99.98% metal purity was procured from Alfa Aesar. Similar material had previously been obtained for use in inelastic neutron scattering studies performed upon deformed PdH_x samples [74, 95, 53, 76]. Before receiving the material, the Pd had been cold-rolled into 0.25 mm thick sheets, creating a polycrystalline structure within which a nominal dislocation density exists. In order to introduce dislocations into Pd beyond those introduced from cold rolling, the samples were pumped with hydrogen across the low concentration phase boundary and subsequently depleted (hydride cycling). As has been discussed elsewhere, the resultant dislocation landscape is an amalgamation of cell-like structures formed due to cold working and a uniform distribution.
contained within the cells due to the hydride cycling process \cite{95}. In the first rendition of this analysis, four sample sets were developed from this material, due to desire to test annealed and deformed samples on both BASIS and HFBS. Two deformed samples were created for BASIS (Def-1 and Def-2), while an annealed sample was created for both BASIS (Ann-1) and HFBS (Ann-2). Def-1 was recycled to create the BASIS annealed sample, following a ten hour annealing process at 1273K in order to fully recover the base FCC structure. Following the annealing, large grains were visible on the Pd sheet surfaces. Def-2 was created using the base material described, but was made using about twice the amount of Pd with a similar level of available H$_2$ during sample creation, leading to a lower absorbed concentration. The sample terminology described above is due to \cite{12} and will be slightly modified to avoid confusion with output from the CNCS instrument; thus Def-1, Def-2 and Ann-1 will be renamed B-Def-1, B-Def-2, and B-Ann, while Ann-2 will become H-Ann. The subsequent CNCS tests, then, will be denoted as C-Def and C-Ann, since a single [H] was tested in this experimental set. The sample parameters and investigated temperatures for each of these tests is demarcated in Table 4.1. The CNCS samples underwent a similar preparation to that of the BASIS and HFBS samples, except that separate samples were used for annealed and deformed tests. For each CNCS sample, the Pd sheet was cut into small strips in order to facilitate correct measurement of sample size. The strips to be used for the deformed sample were roughened in order to improve surface absorption during the cycling process. Each sample described was sealed within a cylindrical aluminum casing with a metal isolation valve, with internal volume of 62.54 cm$^3$. The samples were then attached to hydrogen loading mechanism, in which [H] introduced into each sample for a known Pd mass was found due to H$_2$ gas pressure change using the ideal gas law \cite{88}. The loaded concentration was measured using a temperature-controlled MRS Baratron capacitance manometer (Model 627B, 2 Torr full scale range, $10^{-5}$ Torr resolution), which monitored volumetric changes within the system volume of 1190 cm$^3$ including the volume of the aluminum casing \cite{88}. Hydrogen temperature gradients were eliminated via a helium exchange gas at $\sim$120 mbar, while hydrogen concentration gradients were reduced via elongated holds ($\sim$72 hours) at 350K following the loading process.

4.3 Execution of Experiment and Preliminary Analysis

In performing each experiment, the sample casing was first mounted onto an instrumented sample stick such that the sample would be contained fully within the incident beam from the instrument’s neutron guide. As already described, the neutron wavelength band was centered near 6.267 Å for BASIS, corresponding to a median incident neutron energy of 2.083 meV, while the incident energy
during the CNCS tests was assumed to be nearly monochromatic around 3 meV since the measured prompt pulse width of 11 µeV fell well within the instrumental resolution. A close-cycled refrigerator was then used to modify the temperature. Table 4.1 provides a comprehensive insight into the domain probed by the full breadth of QENS tests performed. It should be mentioned that in some cases, the results obtained refer to the run numbers of the samples, which are labelled accordingly in this table. The lower temperature measurements noted provide the resolution function of the data, since all diffusive motion is restricted at the temperatures tested and thus any sample-dependent resolution effects should then be accounted for. In the case of HFBS and CNCS, a vanadium sample was also taken at a sub-cryogenic temperature in order to validate the application of the instrumental resolution upon the annealed data sets. For CNCS, since the high resolution setting was applied, each tested temperature involved a discrete set of runs on each sample that were conducted until an appropriate proton charge was reached, which was occurred about 2970 seconds after the testing period began for the deformed sample. The MANTID data reduction package [101] was subsequently used to parse the direct instrument output into different file types, depending on the instrument. In the case of BASIS, the data was summed and binned into 9 distinct Q bins (0.3 1/Å < Q < 1.9 1/Å) directly within MANTID, and then processed into an ASCII format yielding a binned intensity distribution over the symmetric energy transfer window for each Q bin. HFBS data underwent a similar process, but 16 discrete bins were used over a similar Q range (0.25 1/Å < Q < 1.8 1/Å). In the case of CNCS, MANTID was applied in order to create .nxspe files representative of the S(Q,ω) distribution across the entire array of detectors available. For further analysis of the CNCS data, the MSlice program within the Data Analysis and Visualization Environment (DAVE) software package [102] was applied. By summing the multi-detector .nxspe files from each run in MSlice, a pixelated map in [Q,ω] space was created in order to provide a preliminary comparison of the C-Def and C-Ann output. As is seen in Figure 4.3, there is a distinct broadening around the elastic line for the deformed sample increasing with Q. On the other hand, this trend is not seen in the annealed sample at the same temperature, as Figure 4.2 demonstrates. Inspection of Figure 4.2 points to the conclusion that the annealed sample tested at 295K appears to have undergone scattering on the order of the “frozen” 10K deformed sample, indicating that the QENS broadening for an annealed sample at near room temperature may actually fall very close to the deformed resolution data obtained on CNCS. Also seen in all of the mentioned figures is the existence of two Q-independent increases in intensity near ΔE of 1.25 and 1.75 meV. These events were noted as spurious during the measurement process, and will be accounted for accordingly in the CNCS analysis. In terms of the BASIS and HFBS data, DAVE was originally utilized in the secondary stages of data analysis in order to perform peak fitting in the energy domain. While this process will be touched upon in Chapter 5, the
following section will relate the steps taken to convert the $S(Q, \omega)$ data procured from each instrument and transform it into the ISF representation.

(a) MSlice Output for Deformed CNCS, 10K

(b) MSlice Output for Annealed CNCS, 295K

Figure 4.2: Summed intensity over $[Q, \omega]$ space, represented as Q vs. Energy, for the low temperature deformed and room temperature annealed CNCS data sets. As can be seen, the QENS broadening for the low T sample and the annealed sample are nearly identical in nature.

Figure 4.3: MSlice Output for Deformed CNCS, 295K. The QENS broadening can be seen to increase in E as a function of Q, clearly indicating that a strong relationship exists to the deformed QENS broadening in this energy domain.
Table 4.1: Tested sample parameters for each QENS instrument utilized (compiled in part via [12]).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Run Number (IPTS)</th>
<th>Pd sample mass (g)</th>
<th>[H]/[Pd] (at. ppm.)</th>
<th>H loading inventory (mg)</th>
<th>Measured Temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-Def-1</td>
<td>6162</td>
<td>116</td>
<td>1130</td>
<td>1.2</td>
<td>20,150,200,250,300,350,400</td>
</tr>
<tr>
<td>B-Def-2</td>
<td>8239</td>
<td>311</td>
<td>520</td>
<td>1.5</td>
<td>15,220,260,300,350</td>
</tr>
<tr>
<td>C-Def</td>
<td>13765</td>
<td></td>
<td>1458</td>
<td></td>
<td>10,250,295,250</td>
</tr>
<tr>
<td>B-Ann</td>
<td>8239</td>
<td>116</td>
<td>2020</td>
<td>2.2</td>
<td>15,200,280,350</td>
</tr>
<tr>
<td>C-Ann</td>
<td>13765</td>
<td></td>
<td>1458</td>
<td></td>
<td>250,295,350</td>
</tr>
<tr>
<td>H-Ann</td>
<td>59</td>
<td></td>
<td>3330</td>
<td>1.8</td>
<td>300,400</td>
</tr>
</tbody>
</table>

4.4 Intermediate Scattering Function: 
Creation and Analysis

As was previously discussed in Chapter 3, the foundation of QENS analysis lies within analyzing the dynamic structure factor via a set of functions fit to the data in the energy/frequency domain. Two critical issues arise due to this method, namely the difficulty of accurately determining the correct ratio of magnitude between the convoluted instrumental resolution and the QENS broadening, as well as the difficulty of extending the measurable experimental energy domain by comparisons between different instrument due to the inherently different operating parameters. Additionally, as was also pointed out in the earlier theoretical discussion, it is naive to describe the QENS broadening due to diffusion events in the near-core region using a Lorentizan as would be typical of a jump diffusion, since this assumes a Bravais lattice configuration that will not be found within this structure. Thus, a computational method was developed for analyzing the intermediate scattering function $F_{\text{inc}}(Q,t)$, as this allows for each of these concerns to be directly addressed. A set of scripts were developed in MATLAB with the intent of conducting the following process:

1) Perform a Gaussian fit to the resolution function for each instrument, which acts as a “smoothed” substitute for the resolution function in the case of any instrumental anomalies.

2) Perform a Fourier transform on the data, in order to change from the energy/frequency domain into the time domain. The code was developed in order to allow for both symmetric and asymmetric Fourier transforms, carried out respectively by the Fast Fourier Transform (FFT) and multiplication of the data by a Fourier coefficient matrix. The data was first shifted such that it was centered on the elastic line. This method was performed due to a slight modification of the deconvolution code created by Professor Yang Zhang of the University of Illinois at Urbana-Champaign.

3) Assess the obtained ISF for each instrument independently, and analyze their outputs simultaneously within the same domain, using a scaling method (if necessary) to create a continuous combined ISF for each Q bin.

The created ISFs were then exported into the curve analysis software of Origin, allowing for customized fitting comparisons to be conducted. Before
this aspect of the analysis was approached, however, it was necessary to address the effect that using different instrumental geometries has on each instrument’s output. As can be seen in Figure 4.4, the output of each instrument type is mirrored due to how each instrument analyzes the data. On BASIS and other indirect geometry instruments, the QENS peak reflects the energy change of the neutron.

![Figure 4.4: Comparison of energy gain and loss within the scattering system on the BASIS (indirect geometry) and CNCS (direct geometry) instruments. As can be seen, BASIS relates positive $\Delta E$ to an upscattering (energy gain) event for the neutron, while CNCS relates positive $\Delta E$ to an energy gain for the scattering system, thus correlating to a downscattering (energy loss) for the scattered neutron.](image)

Therefore, for a positive $\Delta E$, the neutron is undergoing an upscattering event and thus gaining energy from the scattering interaction. On the other hand, the QENS peak output of CNCS reflects a change in the scattering system energy, and a positive $\Delta E$ represents energy lost by the neutron. As a result, the CNCS output has a positive $\Delta E$ range limited by the energy of the incident neutrons, but a negative $\Delta E$ range that can be significantly extended as the neutrons can absorb a much wider range of energy from the scattering system. Also, due to an instrumentation issue on CNCS, there arose a set of spurious peaks within the downscattering (right hand) side of the peak. As can be seen in Figure 4.5, using the a symmetric Fourier transform on the reflected upscattering ($-\Delta E$) data will extend the range of analyzable data beyond the limit of the incident neutron energy, and also avoid unknown detrimental effects due to the spurious intensity. In the case of BASIS, however, the energy transfer window is symmetric while the data is not. A slight shoulder exists on the upscattering region of the BASIS QENS peak, which was seen via comparison of reflections of each part of the peak and the significant effect on the created ISF when using the symmetric method. Thus, in order to avoid incorrectly assessing the ISF, the asymmetric Fourier transform was applied on the BASIS QENS peaks.
In the above described steps, it was mentioned that an analogous resolution function was developed by fitting a set of Gaussians to the instrumental resolution in an effort to eliminate noise when applying FFT. Additionally, noise within the FFT can be reduced by interpolating between the available points before performing the transform. This is not possible while using the asymmetric method, implying that there will in general be a smaller $\Delta t$ between points if the symmetric FT is applied. In an effort to demonstrate that the resolution function was properly removed from the intensity function after the Fourier transform was performed, this resolution function was divided from the transformed data and compared to a similar division using the Fourier transformed instrumental resolution, using the method that was described in detail in Chapter 3. For all cases, the most precise solution will be found via division by the asymmetric Fourier Transform of the true resolution data, since this method makes the fewest approximations to the data. For both the deformed and annealed cases, this method yields the most usable data from BASIS, since the instrument’s inherently asymmetric outputs overwhelms the increase in resolvable data allowed via the symmetric method. In the deformed case, comparison of CNCS yielded the opposite conclusion, with a much cleaner output being created if the upscattering side was reflected over the elastic line. An interesting problem arose when considering the CNCS annealed data, as both analysis methods yielded a peculiar output - a ISF that remained effectively equal to one throughout the entire applicable time range. This would seem to imply that there is exactly no QENS broadening within the detectable resolution of CNCS for an annealed sample. However, it should not be immediately concluded that the annealed sample’s diffusive processes are completely “frozen
out" on CNCS, especially due to the variable effect that using a different resolution function would have. Although the asymmetric version of the annealed process shows frozen motions to about 90 ps, this was not at first completely verifiable since there was not a measurement taken to inspect the resolution function for the annealed sample and thus the deformed version of the resolution was used. The case could be then be made that although diffusive events should not affect the resolution function at the tested temperature (10-15 K), there could still be contributions due to different sample size or variation within the neutron beam leading to additional QENS broadening. In an attempt to remedy this, a set of resolution functions created using a vanadium sample were compared to the annealed CNCS output. After using a single Gaussian to estimate the vanadium resolution data, it was seen that single Gaussian fit led to an invalid estimate of the actual attenuation. The created ISF resembled an exponential decay on the order of the width of the resolution function, implying that the vanadium resolution could be characterized using additional Gaussian curves. As the number of Gaussians was increased, the attenuation across the CNCS time scale converged to one. This lack of attenuation can also be seen if a theoretical exponential decay with a $\tau_{KWW}$ corresponding to a characteristic FWHM from the annealed BASIS analysis in DAVE is created. Within the operational time range of CNCS up to about 90 ps, the attenuation is minute on this time scale, implying that motions would be essentially undetectable. As will be seen in Chapter 5, this lack of attenuation is actually an important indication that more rapid diffusive processes are indeed occurring within the deformed samples. A few other small modifications were to prepare the data for proper ISF analysis. As pointed out by Schiavone et al. [89], there lies an intrinsic issue within the classic single Lorentzian QENS analysis method, in that it misinterprets the valid range of data with the only indicator of an incorrect method resolving itself within uncharacteristically high jump distances. However, by analyzing the data in the time domain, this effect is negated by only permitting data from the resolvable time scale of each instrument. At first, it was assumed that since each instrument had a known energy transfer window, data from each Q bin could be formatted to fit within a single time range. This was realized as a fallacy due to the Q-dependent peaks widths of each instrument’s resolution function seen in the energy domain. As a result, a different method was applied, in which the resolution function’s FWHM was converted to the time domain. Due to the inverse relationship of time and energy resulting from the Fourier transform, small FWHMs correlate to larger times, thus creating a “cutoff function” for the higher time scales of the BASIS and CNCS data. A broadening of the FWHM with increasing Q led to a smaller valid time domain for the larger Q bins. On the other side of the energy transfer spectrum, the symmetry of the BASIS data window implied that the time domain cutoff would be identical on at lower time scales. For CNCS, however, applying the symmetric Fourier transform to the reflected upscattering data at first created
a problematic “ringing” within the smaller Q bins. It was later concluded that since the energy transfer window differed for each Q bin on CNCS, a zero was used as a placeholder when there did not exist data for a specific magnitude of energy transfer. As a result, the data was undergoing a padding effect, which was interpreted through the applied Fourier transform as a sinusoidal frequency within the exponential decay. This issue was resolved by truncating the applicable energy window for the reflected data to a range appropriate to each Q bin.
Chapter 5

Results

5.1 Base Analysis: Isotropically Averaged Chudley-Elliot Model, using DAVE

As is previously mentioned in Chapter 4, the DAVE software package created at NIST [102] was the original tool utilized for analysis of the data obtained from BASIS. While performing the DAVE analysis, a number of assumptions were made about the data due to the inherent restrictions of using the software and the application of the isotropically averaged Chudley-Elliot model. The most crucial of these assumptions is that QENS peak broadening witnessed in both the annealed and deformed samples tested on BASIS could be characterized by fitting either one or two Lorentzians to the data, added to a constant background of intensity and subsequently convoluted with the instrumental resolution obtained for each sample at sub-cryogenic temperatures of 10-20K. Some examples of this initial step of the analysis are presented here as a point of comparison to the newer results.

Figure 5.1: Representation of a typical DAVE fit for B-Ann, with an energy transfer window of ±100µeV. A Lorentzian fit is displayed, and the residual seems to indicate that this is a proper fitting method for the data.
Figure 5.2: Typical DAVE fit for B-Def-1 data at 250K, with an energy transfer window of ±100µeV. A fit of two Lorentzian curves is shown, and the residual shows that this is an acceptable description of the QENS broadening.

Figure 5.3: Typical DAVE fit for B-Def-1 data at 350K, with an energy transfer window of ±100µeV. A fit of a single Lorentzian curve is shown.

Figure 5.1 demonstrates a typical peak fitting model as performed in DAVE on the annealed sample B-Ann at 280K for \( Q = 1.3 \, \text{Å}^{-1} \), whereas Figures 5.2 and 5.3 show the typical format for peak fitting on the deformed sample B-Def-1 at 250K and 350K for the same Q value. The aforementioned fitting method is used for each Q value, while goodness of fit is determined by an examination of the residual plots and a converging chi-squared value as the fits improved. In the annealed case, the single Lorentzian is seen to classify the data well.
at 280K as reflected by the residual plot. For the B-Def-1 deformed case at 250K, the best fits are found using a convolution of two Lorentzian terms with the resolution function. This implies that both a “slow” and “fast” process are visible below 300K, the temperature regime within which dislocation pipe diffusion is expected to occur. Figure 5.3 shows distinction from the fitting method used at 250K in that only a single Lorentzian was utilized in the fitting procedure, even though there is a noticeable residual that could be indicative of an additional Lorentzian term. In attempts to fit the 350K data using an additional Lorentzian term, it was found that another term with a FWHM on the order of the energy transfer window could potentially be used. However, the fitting method frequently provided a “best fit” as the integral area under the second Lorentzian trended to zero, and it was determined that the lowest chi-squared values were found when using a single Lorentzian term alongside a background term. This implies that the “fast” process at 350K needs to be modeled in DAVE by folding the peak broadening into the background term, a direct result of the limited energy transfer window of ±100µeV on BASIS as well as a limitation of the DAVE software.

Figure 5.4: Characteristic plots for the secondary analysis step of the Chudley-Elliot model, via Kaleidagraph. Although the data collected fits well to the C-E model if only the first Lorentzian is inspected, the length obtained from the deformed fits are uncharacteristically high. At the time of publication, further research is necessary in order to investigate this phenomenon [88].

Figure 5.4 demonstrates the usual next step in the QENS analysis in the energy domain for the jump diffusion model, which is to compare the determined FWHM values at each Q to a fit of the Chudley-Elliot model. As discussed in Chapter 3 an anomalous situation arises when the diffusive jump length is taken as a free parameter instead of restricting it to the O-O jump length of 2.75 Å. Although allowing the length of the jump to vary permits the best fits to the experimental data and still gives a cohesive description of diffusivity as given in Heuser et al. [12], the increasing trend in jump length does not logically relate to the actual process within the dislocation, where it is expected that diffu-
sive jumps will occur within higher frequency but at similar or possible shorter lengths for each jump. Schiavone et al. [89] have determined this discrepancy in jump length is directly due to the method of analysis, specifically the use of such a fitting method over an experimentally limited energy window especially when the true nature of the jump is not known to be discrete as is expected in the bulk diffusion model.

Figure 5.5: Dynamic structure factor across 9 distinct Q bins for deformed samples on HFBS, BASIS and CNCS near 300K. Energy transfer window is specified in meV for ease of comparison. The CNCS data is also presented in the symmetric energy window format, making the spurious peaks in the downscattering region of the data more evident.

This discrepancy in jump lengths, as well as the inability to fit the wider Lorentzian term within DAVE, are the primary motivations for the current analysis. Due to the extended energy window on CNCS, it was hoped that the wider component that was not fully captured on BASIS would be ascertained. Instead
of using DAVE to determine the FWHM values for each Q, a code prepared in Matlab is used to analyze the data. Before bridging into the determination of the intermediate scattering function, a comparison of $S_{inc}(Q, E)$ is prepared for each instrument, sample type and temperature tested as described in detail in Table 4.1. Figure 5.5 provides a qualitative comparison of some of the produced $S_{inc}(Q, E)$, using the same energy scale in order to show the differences between the instruments. Each of the subfigures gives the full energy transfer window for each instrument, which significantly varies between HFBS, BASIS and CNCS on scales of $\pm 0.01$ meV, $\pm 0.1$ meV and $\pm 3$ meV respectively if a symmetric window is considered. As shown in the appendix, Figure A.3 clearly displays the differences in instrumental resolution amongst the instruments, which vary similarly to the energy transfer windows. Other notable contrasts exist in the $S_{inc}(Q, E)$ peaks, namely the difference in intensity as compared to system noise for each instrument. Due to the depiction of intensity on log scale, it is clearly visible that the peak intensity of CNCS and BASIS are three orders of magnitude greater than the variance in the data, while the peak intensity of HFBS is only an order of magnitude greater than the background variance for the instrument. It is also clear that the $S_{inc}(Q, E)$ determined for BASIS in Figure 5.5b is asymmetric with regards to the elastic line, implying that the will have to be encountered accordingly when performing the Fourier transformation to the time domain. Figure 5.5c shows the full $S_{inc}(Q, E)$ for C-Def at 295K with the energy transfer window extended up to -10 meV for the upscattering region of the peak, while Figure 5.5d shows a symmetric view of the same data with a domain close to that of the incident 3 meV neutrons used in the experiment. The appearance of two spurious peaks in the downscattering region of the symmetric profile and the much larger energy window gained from the upscattering region leads to a consideration of only the upscattering region when determining $F_{inc}(Q, t)$. Instead of using an asymmetric consideration for the Fourier transformation as was done for BASIS, the upscattering region was reflected across the elastic line and treated with a symmetric FT method. Both methods also take into account the possibility of a slight shift of the experimental elastic line from E=0 by shifting the domain to this point before applying the transform. From this point, the intermediate scattering function of each individual instrument can be determined. The steps taken to ensure data integrity while analyzing different spectrometer’s data will be a key discussion point in the following sections.

5.2 Intermediate Scattering Function

5.2.1 Matlab Analysis

The first step taken in computing the intermediate scattering factor for the instruments in question is performed by applying the method described in Section
in a numerical fashion using Matlab. As is shown in the appended Matlab code, two methods of finding \( F_{inc}(Q,t) \) are applied. The symmetric method applied on the CNCS data involves centering the QENS peak about the elastic line, reflecting the upscattering (-E) region across this line, and performing a fast Fourier transform from the energy domain directly into the time domain via the conversion factor found in Equation 3.37. In order to determine \( F_{inc}(Q,t) \), the newly ascertained time-domain functions I(Q,t) and R(Q,t) are normalized by dividing by the magnitude at \( t=0 \), before dividing each discrete value of I(Q,t) by the corresponding intensity of R(Q,t). In the case of BASIS, the asymmetric method instead calculates the complex Fourier coefficient matrix for both \( S_{inc}(\vec{Q},\omega) \) and \( R(\vec{Q},\omega) \) against a vector of discrete time steps drawn from the energy domain, then applies this matrix transformation to produce complex vectors for I(Q,t) and R(Q,t). The method calculates the modulus of each complex number, then normalizes the real vectors by the value at each function’s first time step. Finally, \( F_{inc}(Q,t) \) is determined by dividing the resulting normalized vectors by each other. It is important to note that each process normalizes the intensity and resolution functions so that no arbitrary scale factor is introduced when dividing the functions in the time domain. In an ideal scenario, where the discrete time domain covers all possible times, this normalization would produce \( F_0 = 1 \), the expected amplitude of the ISF at \( t=0 \) for a purely inelastic scattering. Although an elastic scattering contribution could lead to a nonzero decay process as \( t \to \infty \), when the total magnitude \( F_0(t = 0) < 1 \), it should be considered a limitation of the finite energy window of the experimental setup. Contributions that are generally considered to be part of the background in the energy domain will lead to a variation in the intensity of \( F_0 \) as \( t \to 0 \), as is seen in Figure 5.6. This figure and those that follow in this section also contain red curves indicating the Q-dependent resolution function at each temperature. These show the range over which the instrumental resolution function exists, and have a nearly Gaussian shape that is distorted by the use of the log(t) scale.

The difference in background contribution becomes more apparent when the ISF for each instrument tested is compared at a characteristic Q value, as is shown in Figure 5.7. A number of inherent issues with the raw data are confronted as a result of this initial comparison of the deformed PdH\(_x\) data. Firstly, the existence of significant fluctuations within each instrument’s ISF beyond a characteristic time can be attributed to the inability to resolve data points at times that correspond to energy transfers less than the FWHM of the instrument’s resolution function. This concern was at first resolved by excluding data beyond the visual limit at which the ISF began to diverge using an arbitrary cutoff point. This method is decidedly crude and can be further improved upon as will be shown later. The second obvious flaw is in the uniformity of the obtained ISF for CNCS, an issue which manifests itself primarily in lower Q bins. After some investigation, it was realized that this “ringing” mechanism
Figure 5.6: ISF for BASIS data, both the deformed and annealed samples at comparable temperatures (280K and 300K). It should be noted that the BASIS data seems to indicate that $F_0 \neq 1$ for both samples over this range of Q values.

due to how the fast Fourier transform is processed within Matlab. As is seen in Figure 5.5c, reflecting the upscattering region of CNCS before performing a Fourier transform creates a Q-dependent energy transfer window width, ranging from about $\pm 1.2$ meV for Q1 (Q=0.3 Å) up to $\pm 10$ meV at the upper range of Q values. Since the Matlab program had at first assumed a uniform energy transfer window across Q, the unfilled indices were replaced with a zero value, leading to the existence of an underlying sinusoidal frequency in the data. After varying the range of energies over which the FT is conducted, this issue was resolved. The aforementioned concern of correct scaling due to variation in background terms between the instruments tested is confronted in the Matlab code as well. Unlike a DAVE analysis, in which the inclusion of a nonuniform background term leads to a significant effect on the determination of wider Lorentzian terms, the ISF from BASIS is scaled to match that of CNCS at a point where they both overlap and contain resolvable data. This was likewise done to scale the HFBS ISF to that of BASIS, while the CNCS data remains unscaled. Thus, instrumental differences in background are essentially removed, as is evident in Figure 5.8.

The final glaring problem seen in Figure 5.7 is the quality of the HFBS data, especially in relationship to that of BASIS and CNCS. Even after the initial truncating and scaling processes, the usefulness of the HFBS still comes into question as is clear in Figure 5.8, which shows the initial forms of the combined ISF for some representative Q values, displayed at 300K for both sample types. The measured HFBS data fluctuates wildly especially in the deformed case, and does not follow the trend that is clearly established by the CNCS and BASIS data. This is likely a direct reflection of the large signal-to-noise ratio seen in the characteristic $S_{inc}(Q,E)$ in Figure 5.5a. As a result of poor resolution, the
Figure 5.7: ISF for deformed PdH$_x$ at 350K for each sample set (C-Def, B-Def-1 and H-Def), log(t) scale. This single Q bin of data (Q ≃ 0.55 1/Å) demonstrates the nature of the unscaled data, which is a result of different consideration of near-elastic terms. It also demonstrates the poor resolution of HFBS data for this system.

data obtained from HFBS will be neglected for the rest of the analysis.

Although the corrections mentioned have the potential to be applied to any of the available experimental data sets, a comparison of the physical aspects for the samples shows that C-Def is more likely to have similar diffusive characteristics to B-Def-1 than B-Def-2 due to the similarity in sample size and a relative closeness in [H] between the samples. These samples are have better congruity in their probed temperatures, an important facet of correctly determining what occurs during the transition from DPD to bulk diffusion. To validate this decision of combining the ISF curves for B-Def-1 and C-Def, the obtained ISF for B-Def-1 and B-Def-2 are compared to the CNCS results without background adjustment at each temperature and Q value tested. The unadjusted $F_{inc}(Q,t)$ curves in Figure 5.9b relate the difference between the higher and lower concentration BASIS samples (B-Def-1 and B-Def-2 respectively) as compared to the deformed CNCS sample result at 300K for an intermediate Q value. From
Figure 5.8: Figure 5.8a relates an initial attempt at scaling the data from the three available instruments for annealed data near 300K at $Q = 1.3 \, \text{Å}^{-1}$, indicating that the HFBS data does not follow the trend established by the other instruments. This poor resolution is further demonstrated in the scaled deformed data in Figure 5.8b.

Figure 5.9: Examples of ISF for CNCS/BASIS combined data, annealed and deformed samples. No additional scaling has been performed in this situation, indicating that a difference in $F_0$ exists between the two varied [H] sets in Figure 5.9b.

In this comparison, it appears that unscaled B-Def-1 curve more closely relates to the CNCS sample in terms of $F_0$ value as well as smoothness of the transition period between regimes. Similar agreement between occurs between B-Def-1 and C-Def at 250K and 350K, although the results for both BASIS samples have similar ISFs at 250K. The B-Def-1 is chosen for continued comparison to
the deformed CNCS sample due to their closer physical similarity and the relative agreement of their $F_{inc}(Q,t)$ curves. Figure 5.9a relates similar parameters for the annealed sample comparison, clearly demonstrating that the diffusive motions are essentially “frozen” across the CNCS time domain as well as the continuity of the CNCS/BASIS annealed ISF. It should be noted that Figure 5.9 demonstrates a significant improvement in the resolvability within the $10^4$ ps time domain over the ISFs found from BASIS alone, as can be seen by comparing to Figure 5.6. However, these results still appear poorly constructed at higher times because the resolution of each instrument has not yet been taken into account. As was already mentioned, Figure 5.8 represents an arbitrary truncation attempt, but not a systematic one. A systematic method is easily accomplished by performing a single Gaussian fit to the resolution function of each instrument at each Q value, which can be considered a first approximation of the resolution function shape. After extracting the FWHM of each of these Gaussian fits, the conversion described in Equation 3.37 can be applied, yielding a sample-specific, Q-dependent upper bound on the time domain for each
Once this final method is applied, it is possible to extract fully comparable sets of data combining the resolvable data from CNCS and BASIS. As is shown in Figure 5.11, the gathered data sets from CNCS and BASIS show significant qualitative differences in the ISF attenuation. However, it is elected to conduct quantitative analysis using Origin in order to better quantify the goodness of fit to the various theoretical models discussed in Chapter 3. In the following sections, the data from CNCS and BASIS will be separately analyzed, while neglecting the HFBS data due to the poor resolution in the time domain. Insight into the combined data sets will then be presented, including quality of fit for each proposed decay mechanism for the constructed $F_{inc}(Q,t)$ curves.

### 5.2.2 Separate Instruments

As has been discussed previously, it is possible to determine $F_{inc}(Q,t)$ for each instrument independently, but due to the instrumental restrictions of each technique this is not an ideal solution. The ISFs for the separate BASIS and CNCS scattering experiments are presented here for two purposes: as a point of comparison of the ISF technique to the DAVE analysis, and as a way to further probe the CNCS results to determine what effect choosing a specific Q-bin size in MSlice has upon the quality of the analysis.

Figure 5.12 displays an attempt at fitting the annealed data gathered on BASIS with a single exponential curve, representative of a homogeneous diffusive mechanism in the sample. As can be seen, the exponential fit performed well at a temperature of 280K, but failed to represent the ISF at 350K except at the lowest Q bin of Q=0.3 Å. Further attempts to model this data showed that a pair of exponentials could more successfully be fit to the B-Ann 350K data, implying that there could be a two diffusive mechanisms at this temperature such as both jump diffusion between octahedral sites and slower diffusive path more similar to continuous Brownian motion. The appearance of an additional mode within the ISF can also be seen in the deformed BASIS data and becomes more prevalent at temperatures above 300K. When compared to the C-Ann results at 295K, seen in Figure 5.14, it is evident that nearly no contribution to the exponential decay happens within the resolvable range of the instrument. This lack of attenuation is actually an important indication that more rapid diffusive processes are indeed occurring within the deformed samples, as the C-Def results indicate a significant decay within the CNCS energy transfer window. Figure 5.13 provides the parameter output obtained via Origin for the 280K exponential fits on the B-Ann data, including a quantitative comparison of the goodness of fit for each Q bin. The goodness of fit can be classified using the reduced chi-squared and adjusted coefficient of determination values, which give different measures of the correlation between the data and the model selected. Also known as r-squared, the coefficient of determination relates the quality of
Figure 5.11: Processing done in Matlab leads to scaled and truncated data as seen above. The deformed data set at 300K will be compared to the 250K and 350K sets, as well as qualitatively to the annealed 295K/280K and 295K/350K sets.

(a) $F_{inc}(Q,t)$ for C-Ann 295K/B-Ann 280K, log(t) scale.

(b) $F_{inc}(Q,t)$ for C-Def 295K/B-Def-1 300K, log(t) scale.

(c) $F_{inc}(Q,t)$ for C-Ann 295K/B-Ann 280K, linear time scale.

(d) $F_{inc}(Q,t)$ for C-Def 295K/B-Def-1 300K, linear time scale.

A fit by providing a percentage of the data’s variance from the mean expected value that can be classified using the regression model. For example, when r-squared is at the maximum value of one, this implies that the fit used suitably models the response data within the variance of each data value. The adjusted r-squared values are scaled in order to remove the effects of different amounts of discrete data points within a set, implying that this metric can be used to compare the goodness of fit across differently truncated data sets. In addition to comparing the absolute goodness of fit, the adjusted r-squared value is scaled according to the number of free parameters in the model, implying that it acts as a sufficient method for comparing models across the same data sets. This
Figure 5.12: ISF of B-Ann, without truncation. As is seen, a single exponential fit, analogous to a Lorentzian in the energy domain, performs rather well in describing the 280K data but not the 350K data.

Method of describing goodness of fit is directly reliant upon the error at each data point of the ISF, which is not immediately depicted in Figures 5.12 and 5.15. While instrumental error does exist at each data point in the energy domain as is seen in the earlier figures of $S_{inc}(Q,E)$, significant difficulty arises when attempting to classify the contributions made to this error once the Fourier transform has been performed. However, due to the high counting statistics on both BASIS and CNCS which limited the signal to noise ratio near the elastic peak to less than one percent for both instruments, the variation in error contribution is assumed to be insignificant across the time domain. Instead, in the context of the ISF, it is assumed that constant error exists for each data point and that the intensity of error bars associated with each point reside within the range of the point itself. This still allows for a goodness of fit comparison to be carried out, as the variance at each data point will have a limited effect on the goodness of fit and different fit types will be independently compared on individual Q bins.

Figure 5.13: Example of a summary of fitting parameters obtained from Origin, specifically for the B-Ann fits at 280K using a single exponential.

Figure 5.15 also displays a comparison of varied choices of Q bin for the C-Def data, independent of the BASIS results. As the data was originally binned in MSlice to match the $\Delta Q$ of the BASIS results, this comparison was made to both inspect goodness of fit for the stretched exponential model over the CNCS time domain, and to see if a change in bin size would directly affect the
result. The comparison here shows stretched exponential fits, where both the $\tau_{KWW}$ and $\beta_{KWW}$ parameters are allowed to vary, and indicate that this is an excellent fit to the ISF over this time domain. In the course of this comparison, the average values of $\beta_{KWW}$ found were congruent for both choices of $\Delta Q$, equivalent to $\beta_{KWW}=0.55$ for $\Delta Q=2.0 \text{ Å}^{-1}$ and $\beta_{KWW}=0.56$ for $\Delta Q=2.0 \text{ Å}^{-1}$ at 350K. Similar agreement is seen in the results at 250K and 300K. Comparing the fits of Figures 5.15a and 5.15b with Figures 5.15c and 5.15d, it is clear that while allowing for $\beta_{KWW}$ to vary provides the best fit to the data, choosing an average $\beta_{KWW}$ value is still a feasible way to model the results, as there is only a minor discrepancy in the fits at times around 1 ps for higher Q values. In order to simultaneously characterize the data from each instrument and to avoid any instrumental anomalies that could be caused by using smaller Q bins, $\Delta Q=2.0 \text{ Å}^{-1}$ was chosen for the combined data analysis.

To further enhance the claim for the applicability of the stretched exponential in describing the ISF obtained from CNCS, Figure 5.16 presents a set of fits performed on a single Q bin for C-Def at 350K. As can be seen, a single exponential ($\beta_{KWW}=1$) does not fully replicate the ISF decay, while a fit using the average value for this temperature of $\beta_{KWW}=0.55$ yields a fit with good agreement to the data. The fitting process conducted here verifies that the stretched exponential is an effective description for the ISF decay on C-Def, while the lack of ISF attenuation on C-Ann indicates that this same diffusive mode is not seen in the annealed sample. Quantitative parameters are obtained
Figure 5.15: Investigation of effects of Q bin size on the fitting parameters for C-Def data. \( \Delta Q = 2.0 \text{ Å}^{-1} \) is chosen to be the same as that of the BASIS instrument, while the \( \Delta Q = 1.0 \text{ Å}^{-1} \) is analyzed for comparison. Little effect is seen on the average \( \beta \) value across the range of temperatures tested.

from the fits of C-Def results, but an anomaly occurs in the magnitude of the \( \tau_{KWW} \) values that leads to comparable FWHM values that are \( 10^4 \) orders of magnitude smaller than are expected. It should be recalled that the DAVE fits of \( S_{inc}(Q,E) \) for B-Def-1 demonstrate an additional QENS broadening with a FWHM on the order of the BASIS energy transfer window (\( \sim 10^3 \mu eV \)), while this initial analysis of the C-Def results seems to provide an erroneously small FWHM on the order of \( 10^{-1} \mu eV \). This significant discrepancy can be explained using a concept known as the e-folding time. When classifying an exponential curve using the functional form \( \exp(t/\tau) \), the value of \( \tau \) is defined by the length of time over which it takes the function to decay to 1/e of the original intensity. As the results from C-Def have shown, the determined ISFs decay to only about 75 percent of the original intensity across the resolvable time domain, while requiring a decay to approximately 37 percent of the original intensity to be considered properly characterized. Thus, although the value of \( \beta_{KWW} \) can...
be used to classify the shape of the ISFs, it is prudent to combine the results from BASIS and CNCS in order to gather a more quantitative picture of the ISF decay across a wider time domain.

5.2.3 Simultaneous Analysis from CNCS and BASIS

With the previously discussed methods for proper comparison of ISF results from different spectrometers, it is now possible to present an analysis of the results combined from BASIS and CNCS. As is expected from the earlier discussion on the lack of attenuation in the ISF for C-Ann, the exponential decay from BASIS dominates the resulting fits. Figure 5.17 shows the ISF for the entire resolvable time domain of BASIS/CNCS, fit using a single exponential decay. The decay parameters attained from this method are very similar to those presented in Figure 5.13, while the goodness of fit was improved amongst all Q bins except for Q1. The associated fitting parameters for this set of fits and the other fits to be discussed here are attached in the Appendix. Figure 5.18a relates the poor reliability of a single exponential mode for describing the combined annealed ISFs at 350K, while Figure 5.18b uses a sum of two exponential to describe the ISF and provides a more accurate fit to the results. It should be noted that the CNCS data has been scaled such that the first data point is equal to one for the purposes of the annealed analysis. As is seen earlier in Figure 5.14, it is difficult to distinguish any attenuating behavior in the

![Diagram of CNCS Deformed 350K, Single KWW](image)

Figure 5.16: ISF for C-Def at 350K, Q=1.1 Å⁻¹, fit with an array of stretched exponentials with fixed β.
ISFs because each ISF approaches a different initial value close to 1. Since any value of the ISF greater than one is considered erroneous since this implies the QENS broadening is less than that at “frozen” temperatures, the ISF can be appropriately scaled to converge to unity at t=0. While attempts were made at resolving this discrepancy using an instrumental resolution from a vanadium sample, the results were similar enough to be disregarded. By choosing the same origin point for each annealed ISF, each function is able to be fit using a single exponential with $F_0=1$. Also, due to the difference in temperature between the gathered B-Ann/C-Ann results, the temperature of measurement is presented for both tests along with an average temperature that allows for a qualitative description of the ISF behavior below and above the 300K benchmark.

![ISF for BASIS 8239/CNCS 13765](image)

Figure 5.17: Origin fit of combined annealed results at average temperature of 288K, untruncated and fit with a single exponential term

In the analysis of the combined BASIS/CNCS results for the deformed samples, a set of different characteristic fit types are compared against each other in order to determine the best model for the data. As will be seen, although the different fit types all show relatively good agreement with the data, the highest quality of fit is attained when a stretched exponential decay is applied to the region of the ISF attributed to the more rapid diffusive modes expected from DPD. In each of the fits in Figures 5.19 and 5.21, the data is shown in an untruncated form on a log(t) time scale. In this context, the untruncated form implies that the entire resolvable time domain of CNCS/BASIS is included in the fitting process. In Figure 5.19, the red line represents a single stretched
(a) Origin fit of combined annealed results at average temperature of 322K, untruncated and fit with a single exponential term.

(b) Origin fit of combined annealed results at average temperature of 322K, untruncated and fit with two exponential terms.

Figure 5.18: Model comparison for higher temperature annealed results, combined from both instruments. The poor agreement when using a single exponential term exists due to another contribution to the ISF at larger time scales.

exponential of variable $\beta$ used to fit the entire data range, while the blue line in Figure 5.20 represents a fit of two exponential terms ($\beta=1$) with varying $\tau_{KWW}$ values. The black line in Figure 5.21 indicates a fit of a stretched exponential term added to a single exponential ($\beta=1$) term, with freedom allowed for different $\tau_{KWW}$ values. This color scheme is used in Figures 5.22, 5.23, and 5.24 to represent similar fit types near 300K, and repeated in Figures 5.25, 5.26, and 5.27 for 350K. Additionally, the summary Figures 5.28, 5.29, and 5.30 use this general fitting scheme to compare the quality of fit types against each other directly. As another point of comparison, the results and the accompanying models are presented on a linear time scale in Figure 5.31 in order to enhance the appearance of goodness of fit within the BASIS time domain.

From this set of figures, many important qualitative conclusions can be drawn. In Figure 5.19 at 250K, it is clear that the single stretched exponential fit does a sufficient job of describing the general decay mechanism in the ISFs, but the model overestimates the ISFs at low times of less than 5 picoseconds. On the other hand, using a sum of two exponentials as is done in Figure 5.20 seems to underestimate the ISF of the DPD region, an effect that becomes more significant as $Q$ increases. This is a logical trend due to the inverse relationship between momentum transfer and real space. Lower $Q$ values model diffusive behavior that correlates with the $DQ^2$ relationship discussed in Chapter 3 and as such will appear to have a mode in the DPD region closely represented by a Lorentzian as this is likely indicative of long range continuous diffusion. On the other hand, as was previously shown in Figure 5.16 high $Q$ values that more closely reflect the short range diffusive modes within the core can only be well represented by a stretched exponential that is equivalent to a heterogeneous diffusive mechanism occurring within the core and near-core region. Thus, it is logical for the qualitatively best fit at 250K to be well described using the
Figure 5.19: $F_{inc}(Q, t)$ for combined deformed sample results at 250K, fit using a single stretched exponential across the entire resolvable time domain.

The sum of a single exponential and a stretched exponential with variable $\beta_{KWW}$ that decreases as a function of $Q$, which Figure 5.21 clearly demonstrates. In consideration of the modeled fits at 300K, there is a notable loss in the capacity of the single stretched exponential to characterize the entire resolvable domain, while this fitting method fails spectacularly at 350K. When using a double exponential fit at 300K, only Q1 and Q2 can be acceptably characterized, while fits at the other Q values yield significant underestimation of the ISF at small t. This issue is compounded at 350K, and it can be seen in Figure 5.26 that using a double exponential fit also detracts from the nature of the exponential decay in the BASIS time domain due to overcompensation of reducing error for the CNCS regime. As Figure 5.24 and 5.27 display, there is a significant shift of the range of time over which a stretched exponential can be utilized. This decrease in the width of the DPD time domain can be directly attributed to an increase in scattered H undergoing bulk-like jump conditions, but the quality of fits seen in these figures for the stretched-single exponential sum indicates that some H is still interacting with the deformed region of the Pd lattice even after the depopulation temperature is reached. There is a striking similarity between the ISFs seen for annealed (Figure 5.18b) and deformed (Figure. 5.27) for $t \geq 800$ ps at temperatures above 300K, which is likely attributable to bulklike diffusive modes in both samples. It is likely that two separate diffusive modes exist in the annealed sample above 300K, both of which resemble a “uniform”
Figure 5.20: $F_{inc}(Q, t)$ for combined deformed sample results at 250K, fit using a sum of two exponentials of $\beta_{KWW} = 1$ across the entire resolvable time domain.

diffusive mechanism.

The summary Figures lock in on the Q-dependence of goodness of fit for the various fit types, and indicate that fitting discrepancies become exaggerated as temperature increases. The success of the stretched-single exponential model over the untruncated time domain encourages another type of ISF system analysis. As has been already seen, the domain of times covered by each ISF can be manipulated in order to remove unresolved data, a feature which can be utilized to independently analyze a single diffusive mode as long as the correct truncation is chosen. In the cases of Figures 5.32, 5.33 and 5.34 the BASIS region of the resolvable time domain was truncated in order to sufficiently remove the diffusive modes covering larger times, i.e. until a single stretched exponential could be said to well characterize the entire domain. These figures are shown on a linear time domain to distinguish the time domains applied, which deteriorates from a strongly correlated fit up to 300 ps on the 250K results down to a satisfactory fit of the 350K results across a 200 ps range. While modeling the data using the $\beta_{KWW}$ obtained from these truncated stretched exponential fits proved unsuccessful as shown in Figure 5.35 likely due to the aforementioned e-folding equilibrium concern, a strong fit to a stretched exponential including both the CNCS and BASIS results at 250K surely indicates that both instruments are necessary in order to properly classify the system’s diffusive modes. Although this method proved unsuccessful, a strong correlation is found when
Figure 5.21: $F_{inc}(Q, t)$ for combined deformed sample results at 250K, fit using a sum of a stretched exponential of variable $\beta_{KWW}$ and a single exponential of $\beta_{KWW} = 1$. Considering a stretched-single exponential sum where the $\beta_{KWW}$ is fixed to the predetermined average value for that temperature. This relationship is shown in Figure 5.36 for 350K, and the quality goodness of fit suggests that using a fixed average $\beta_{KWW}$ value while varying $\tau_{KWW}$ will still yield a correct result except at the largest of Q values.

A comparison of the mean relaxation time to the residence time is possible as long as a model exists relating HWHM to Q. It is conceivable that with the two central parameters gained from the stretched exponential term and the relaxation time from the single exponential term, the intermediate scattering function $F_{inc}(Q, t)$ will characterize the entire range of diffusive processes occurring at a certain temperature. Further consideration to this characterization will be given in the following section.
Figure 5.22: $F_{\text{inc}}(Q, t)$ for combined deformed sample results at 300K, fit using a single stretched exponential across the entire resolvable time domain.

Figure 5.23: $F_{\text{inc}}(Q, t)$ for combined deformed sample results at 300K, fit using a sum of two exponentials of $\beta_{KWW} = 1$ across the entire resolvable time domain.
Figure 5.24: $F_{inc}(Q, t)$ for combined deformed sample results at 300K, fit using a sum of a stretched exponential of variable $\beta_{KWW}$ and a single exponential of $\beta_{KWW} = 1$.

Figure 5.25: $F_{inc}(Q, t)$ for combined deformed sample results at 350K, fit using a single stretched exponential across the entire resolvable time domain.
Figure 5.26: $F_{inc}(Q, t)$ for combined deformed sample results at 350K, fit using a sum of two exponentials of $\beta_{KWW} = 1$ across the entire resolvable time domain.

Figure 5.27: $F_{inc}(Q, t)$ for combined deformed sample results at 350K, fit using a sum of a stretched exponential of variable $\beta_{KWW}$ and a single exponential of $\beta_{KWW} = 1$. 
Figure 5.28: Origin Fits of combined $F_{inc}(Q, t)$ results, deformed sample at 250K, untruncated, log(t) time scale.

Figure 5.29: Origin Fits of combined $F_{inc}(Q, t)$ results, deformed sample at 300K, untruncated, log(t) time scale.
Figure 5.30: Origin Fits of combined $F_{inc}(Q, t)$ results, deformed sample at 350K, untruncated, log(t) time scale.
(a) Origin Fits of combined ISF results, annealed at 250K, untruncated, linear time scale.

(b) Origin Fits of combined ISF results, deformed at 250K, untruncated, linear time scale.

(c) Origin Fits of combined ISF results, deformed at 300K, untruncated, linear time scale.

(d) Origin Fits of combined ISF results, deformed at 350K, untruncated, linear time scale.

Figure 5.31: Origin Fits of combined ISF results, using same color scheme for deformed fits as in Figure 5.28
Figure 5.32: Origin Fits of combined ISF results, deformed at 250K, truncated, linear time scale. A fit for a single stretched exponential of variable $\beta$ is shown, as it is expected that this region can be analyzed separately from the bulk diffusion region.
Figure 5.33: Origin Fits of combined ISF results, deformed at 300K, truncated, linear time scale.

Figure 5.34: Origin Fits of combined ISF results, deformed at 350K, truncated, linear time scale.
Figure 5.35: Unsuccessful Origin fit of combined ISF results, deformed at 350K, untruncated, log(t) time scale, using a single-stretched exponential sum with a fixed $\beta_{KWW}$ derived from the truncation for each Q.

Figure 5.36: Origin fit of combined ISF results, deformed at 350K, untruncated, log(t) time scale, using a single-stretched exponential sum with a fixed $\beta_{KWW}$ derived from the average $\beta_{KWW}$ for each Q.
In this chapter, a deeper quantitative insight into the quality of the fitting procedures applied in Chapter 5 is presented. The fitting parameters obtained from these processes are discussed, including the characteristic trends seen within the results. As was previously mentioned, comprehensive data regarding the fitting parameters and the quality of fits for individual tests are found in the Appendix, while a summary of the fitting process and some of the key parameters are presented here. The characteristic trends seen are then compared against the results originally obtained from the DAVE analysis, and explained in the context of the deformed PdH\textsubscript{x} system as is alluded to in the theoretical development of Chapter 3. Table 6.1 relates the average $\beta_{KWW}$ values that were found while analyzing the C-Def data independently, and confirms the earlier assertion that correlating $\Delta Q$ with the binning of the B-Def-1 data provides similar values to those found when using the smaller Q bins. It is interesting to note that there is a marked increase in $\beta_{KWW}$ that occurs between 295K and 350K, which can be explained as a return to a more bulk-like diffusive state within the CNCS energy transfer window once hydrogen has begun to depopulate the dislocation traps. The trends seen in Table 6.2 agrees with those seen in the independent C-Def results, in that $\beta_{KWW}$ increases significantly at 350K. Table 6.2 provides the average $\beta_{KWW}$ values found for the three fit types in which a stretched exponential is applied. While the average values found from fitting the entire resolvable domain with a stretched exponential show a maximum at 300K, this is likely an incorrect assessment of the true trend due to the poor KWW fits seen at this temperature. On the other hand, truncating the BASIS region of the results and using a stretched exponential to fit the remaining data leads to an increasing trend from 250K to 350K, which is a more feasible relationship. Using a single-stretched exponential combined fit leads to much larger values for $\beta_{KWW}$, but due to the significant increase in quality of fit over the CNCS time domain as well as agreement with the trend seen in the independent C-Def fitting process, these values can be considered more trustworthy. While the average value of $\beta_{KWW}$ increases from 300K to 350K, it decreases between 250K and 300K. This change can also be explained by the relationship between $\beta_{KWW}$ and the heterogeneity of the diffusive modes in the system. As the temperature increases up to the depopulation temperature, a wider spectrum of
Table 6.1: Average $\beta_{KWW}$ values obtained from C-Def analysis with varying $\Delta Q$.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta Q = 1.0 \ A^{-1}$</th>
<th>$\Delta Q = 2.0 \ A^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Def 250K</td>
<td>0.45</td>
<td>0.47</td>
</tr>
<tr>
<td>C-Def 295K</td>
<td>0.45</td>
<td>0.44</td>
</tr>
<tr>
<td>C-Def 350K</td>
<td>0.56</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 6.2: Average $\beta_{KWW}$ values obtained from combined results analysis.

<table>
<thead>
<tr>
<th></th>
<th>KWW</th>
<th>Trunc. KWW</th>
<th>Exp./KWW</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Def/B-Def-1 250K</td>
<td>0.299</td>
<td>0.285</td>
<td>0.574</td>
</tr>
<tr>
<td>C-Def/B-Def-1 300K</td>
<td>0.336</td>
<td>0.349</td>
<td>0.533</td>
</tr>
<tr>
<td>C-Def/B-Def-1 350K</td>
<td>0.301</td>
<td>0.375</td>
<td>0.634</td>
</tr>
</tbody>
</table>

jump frequencies is introduced within the complex dislocation structure. This leads to a decrease in $\beta_{KWW}$ that contrasts the increase from 300K to 350K, which occurs as a greater percentage of hydrogen begins to undergo the expected jump diffusion process. It should be noted that these average $\beta_{KWW}$ values do not include the fit of Q1 ($Q = 0.3 \ \AA^{-1}$) due to the poor quality found while using stretched exponential fits at low Q values. As will be illustrated in this Chapter, it appears that there is a strong inverse Q dependence in $\beta_{KWW}$, culminating in best fits at low Q values when the variable $\beta_{KWW}$ reaches its maximum constraint of $\beta_{KWW}=1$, which is likely because low Q values relate long-range diffusive modes and it is more likely for hydrogen DPD to appear as Chudley-Elliot jump diffusion over longer diffusion paths.

Table 6.3 details the adjusted $R^2$ values found for each fit type tested for the deformed sample results. These values are extremely close to each other due to the broadness of the resolvable time domain (on the order of $10^3$ picoseconds) and the large number of discrete data points per Q value. However, comparing the adjusted $R^2$ values in order to assess quality of fit is still an acceptable metric because it removes contributions from an increase in the degrees of freedom within the fitted parameter space. Since it is difficult to distinguish improvements in these values due to their closeness to $R^2=1$ (a fit within which the model is able to describe all variance within the system), a simple metric was created to compare the quality of fit. The degree of improvement (DOI) provides an intuitive comparison of two $R^2$ values using the relationship

$$\text{Degree of improvement (DOI)} = \frac{(1 - R^2_{\text{worse}}) - (1 - R^2_{\text{better}})}{1 - R^2_{\text{worse}}} \quad (6.1)$$

The DOI works such that an improvement of the fit to an adjusted $R^2$ value of $R^2=1$ leads to a DOI=1, while comparing two other adjusted $R^2$ values yields a value between 0 and 1 that increases as the degree of improvement of the model
Table 6.3: Adjusted $R^2$ values for combined fits of deformed sample data.

<table>
<thead>
<tr>
<th></th>
<th>KWW</th>
<th>Trunc. KWW</th>
<th>Two Exps.</th>
<th>Exp./KWW</th>
<th>Exp/KWW Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Def/B-Def-1 250K</td>
<td>0.99303875</td>
<td>0.9943875</td>
<td>0.99738375</td>
<td>0.9980275</td>
<td>0.9981375</td>
</tr>
<tr>
<td>C-Def/B-Def-1 300K</td>
<td>0.992655</td>
<td>0.99212375</td>
<td>0.99632625</td>
<td>0.9973225</td>
<td>0.99758</td>
</tr>
<tr>
<td>C-Def/B-Def-1 350K</td>
<td>0.983975</td>
<td>0.98762875</td>
<td>0.9967775</td>
<td>0.9977</td>
<td>0.99817625</td>
</tr>
</tbody>
</table>

Table 6.4: Improvement of each model, compared using the metric developed in Equation 6.1. From left to right is model used to improve fit and degree of improvement.

<table>
<thead>
<tr>
<th></th>
<th>KWW-Trunc. KWW</th>
<th>Two Exps.</th>
<th>Exp./KWW</th>
<th>Exp/KWW Avg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-Def/B-Def-1 250K</td>
<td>0.1896211169</td>
<td>0.5716818081</td>
<td>0.065002032</td>
<td>0.09617180205</td>
</tr>
<tr>
<td>C-Def/B-Def-1 300K</td>
<td>0.06744961117</td>
<td>0.5093601089</td>
<td>0.2570239334</td>
<td>0.09617180205</td>
</tr>
<tr>
<td>C-Def/B-Def-1 350K</td>
<td>0.2280031201</td>
<td>0.7395170254</td>
<td>0.2862684251</td>
<td>0.207052174</td>
</tr>
</tbody>
</table>

increases. As is seen in Table 6.4, the DOI does a much better job of relaying the improvements made per fitting method than the raw adjusted $R^2$ values. From left to right, the stretched exponential fit is more successful over the entire resolvable time domain for 250K, while it performs better over a truncated time domain at 300K and 350K. Using a sum of two exponentials shows a significant improvement in the quality of the fit, which is to be expected because the DPD modes can be (somewhat closely) approximated using a single Lorentzian as was done historically as well as in the DAVE analysis. Transitioning from a sum of two exponentials to a stretched/single exponential fit gives a DOI that increases from 0.184 for 250K to 0.286 for 350K, showing that this fitting method makes a much bigger difference when the DPD diffusive modes and the bulk-like modes have begun to dissociate from each other. Interestingly, using a stretched/single exponential fit while constraining the $\beta_{KWW}$ values to those listed in the third column of Table 6.2 gives the best possible fit for all three temperatures, although the improvement is much less at 250K and 300K. This is likely because the refinement includes one less free parameter and using the average $\beta_{KWW}$ gives characteristically good fits as was seen in Figure 5.16. While it was briefly investigated as to whether the truncated component (the BASIS results in the range between the truncation point and the end of the resolvable domain) can be considered useful data if independently modeled using a single exponential fit, the fits were inconclusive due to the limited domain of usable data. However, if the HFBS results had maintained a lower signal-to-noise ratio, an ISF analysis of this time domain may have led to a more successful attempt.

6.1 Characteristic Trends

The primary characteristic trends seen in the data are an inverse relationship between $\beta_{KWW}$ and Q as well as $\tau_{KWW}$ and Q, while temperature increases
lead to the previously described change in $\beta_{KWW}$, namely minimum values at 300K with significantly higher values at 350K. Figure 6.1 shows the $\beta_{KWW}$ values obtained from the stretched exponential fits, while Figure 6.2 provides the value for $\beta_{KWW}$ in the stretched/single exponential case. The mean $\tau$ values seen in Figure 6.3 yield the FWHM values of Figure 6.4 and 6.5 which demonstrate a good agreement between the isotropic Chudley-Elliot model and the diffusive mode in the annealed sample. The truncated time domain for the higher temperature annealed results may better resemble the postulated results in [89] for annealed PdH$_x$. Figure 6.6 shows the $\tau_{KWW}$ values found for the stretched exponential fits, demonstrating that $\tau_{KWW}$ has the opposite behavior as the expected FWHM behavior. Figure 6.7 indicates the obvious distinction between the values of $\tau_{KWW}$ when a sum of terms is used to model the results, but also shows that the values are relatively similar amongst all of the model types. Figures 6.8 and 6.9 show the $<\tau>$ behavior for the varied $\beta_{KWW}$ stretched-single exponential fits, while Figures 6.10 and 6.11 show the $<\tau>$ behavior when $\beta_{KWW}$ is fixed to an average value. Similar trends are seen, but significant divergence from this trend occurs at Q8 (Q = 1.7 Å$^{-1}$) in the varied $\beta_{KWW}$ results, which can be related to the significant drop in $\beta_{KWW}$ at this Q value as is seen in Figure 6.2. While the FWHM values found from the truncated stretched exponential fits (Figure 6.12) do not yield an encouraging trend that correlates with what is expected for the system, the increasing FWHM vs. Q trend gathered from the stretched exponential component of the averaged $\beta_{KWW}$ fits (Figure 6.13) indicates that this is an appropriate model for this system. It appears that as the temperature increases, the FWHM behavior for the stretched exponential approaches something similar to that of the expected Chudley-Elliot jumps, indicating that a larger percentage of hydrogen is undergoing more bulk-like jumps at this temperature. It should be noted that the FWHMs obtained here seem to correlate well with the large FWHMs predicted by the initial BASIS analysis in DAVE, and indicate jump frequencies on the order of $10^{-12}$ picoseconds, while the single exponential FWHM values of Figure 6.14 indicate jump frequencies on the order of $10^{-10}$ picoseconds as was originally predicted from the BASIS results. It can be concluded that the much more rapid jump frequencies are correlated with a stretched exponential mode because this is a characteristic of the DPD diffusive modes, i.e. an array of jumps exist within the dislocation core that are two order of magnitude more frequent than is seen in the bulk Pd. Although the trends seen in Figure 6.14 are not well established for the slower diffusive mode, this behavior could be improved by increasing the resolvable time domain using an instrument with an energy resolution similar to HFBS but with a lower signal-to-noise ratio. We can tell from the annealed results that a fit of the truncated time domain gives the best behavior on the FWHM vs. Q graphs and does a good job reflecting the results from DAVE, but may not be giving the whole story at the higher temperature range. It appears that the best concept for FWHM vs. Q in the
A deformed fitting procedure is to use averaged $\beta_{KWW}$ single/stretched exponential fits, because the truncated stretched exponential fit does not adequately meet the e-folding time even with the addition of the BASIS data. Another success of the single/stretched exponential fits is that the expected correspondence is seen between the stretched exponential mode and a larger FWHM. It is likely that the energy transfer window of CNCS and the upper limits of the window of BASIS covers the dominant DPD region, while the rest of the resolvable BASIS domain is the bulk regime, which is enhanced as temperature increases and more bulk-like diffusion occurs. Even though the fits of FWHM vs. Q for the single exponential obtained using when an averaged $\beta_{KWW}$ are unjustifiable because the resolved time domain is not as extensive as required, they still allude to a shift from an extended KWW-like regime with a characteristically smaller jump length (as mentioned in [89]) to something that closer resembles a bulk diffusion mode.

**Figure 6.1:** $\beta_{KWW}$ versus Q for stretched exponential fits of the deformed sample results evaluated for different time domains, confirming inverse relationship with increasing Q. However, an incorrect relationship most likely exists in regards to increasing temperature.
Figure 6.2: $\beta_{KWW}$ versus Q for single/stretched exponential fits of the deformed sample results, confirming inverse relationship with increasing Q and characteristically lower values at 300K.

Figure 6.3: $<\tau>$ values for the combined annealed results, fit using a single exponential.
Figure 6.4: FWHM compared to Q for the lower temperature annealed results, well approximated using the isotropic Chudley-Elliot model. Compared to the results obtained from DAVE, the inclusion of the CNCS data has seemingly improved the applicability of the C-E model.

Figure 6.5: FWHM compared to Q for the lower temperature annealed results, with similar values seen to the DAVE analysis if a truncated time domain is applied. This is also approximated using the isotropic Chudley-Elliot model.
Figure 6.6: $\tau_{KWW}$ versus Q for stretched exponential fits of the deformed sample results evaluated for different time domains. Inverse relationship with Q exists, but results differ at higher Q values.

Figure 6.7: $\tau_{KWW}$ versus Q for all fits of the deformed sample results, log scale. Obvious distinction between the values for the two $\tau_{KWW}$ terms exists, even though fits all differ.
Figure 6.8: $\langle \tau \rangle$ versus Q for single/stretched exponential fits of the deformed sample results, log scale. This $\langle \tau \rangle$ correlates to the stretched exponential component of the fit. Significant divergence from the expected decay trend occurs at Q8, possibly correlated with relationship between this Q value and the average DPD jump length.
Figure 6.9: $\tau_{KWV}$ versus Q for single/stretched exponential fits of the deformed sample results, log scale. This $<\tau>$ correlates to the single exponential component of the fit.

Figure 6.10: $<\tau>$ versus Q for single/stretched exponential fits of the deformed sample results, using average $\beta_{KWV}$ values. These values correspond to the stretched exponential component.
Figure 6.11: $<\tau>$ versus $Q$ for single/stretch exponential fits of the deformed sample results, using average $\beta_{KWW}$ values. These values correspond to the single exponential component.

Figure 6.12: FWHM versus $Q$ for stretched exponential fits of the deformed sample results over truncated time domain. The decreasing FWHM trend indicates that this is not a sufficient method for describing the results.
Figure 6.13: FWHM versus Q for single/stretched exponential fits of the deformed sample results, using average $\beta_{KWW}$ values. These values correspond to the stretched exponential component, and show a surprising agreement with the Chudley-Elliot model. The existence of a significantly wider FWHM in the BASIS results is also confirmed.
Figure 6.14: FWHM versus Q for single/stretch exponential fits of the deformed sample results, using average $\beta_{KWW}$ values. These values correspond to the single exponential component, and show similar trends at 250K and 300K. It is likely that the poorly defined increase in FWHM at 350K is due to the limited resolvable domain that could be fit.
6.2 Relation to Theoretical Development

It seems that the bulk-like jumps occurring at 350K are what was primarily witnessed in the DAVE analysis, whereas both jump types were witnessed in the 250K BASIS results because both fell within the BASIS energy transfer window. While the dislocation structure discussed in [12, 89] can be described computationally using a stretched exponential fits that applies to the entire range, it is possible that this is due to the limited dimensions of the created dislocation, modeling the strain field immediately around the dislocation but not the transition into a bulk-like state. Considering both the near-core and inner core regions, the combined strain field leads to a variation in the diffusion process that is proportional to both changes in temperature and Q. The incorrectly long jump lengths found while performing the single Lorenztian Chudley-Elliot fits in [12] are reflective of this transition. As Q increases, the decrease in $\beta_{KWW}$ implies a greater rate of strain interaction within the inner core region. This decreasing $\beta_{KWW}$ indicates that a transition occurs from near-core diffusive modes to those of the inner core as the interatomic distance is approached. This directly explains why lower Q values see good fits to a single or pair of exponentials, while the relatively low $\beta_{KWW}$ and high FWHM seen at Q=1.7 Å$^{-1}$ indicates that this might be the point at which DPD processes are at a maximum. Using the theory discussed in Chapter 3 relating discrete jump frequencies based on the dislocation structure can be applied to these experimental results, but the discrete nature of this model will likely yield different results, especially since this discrete model does not take into account the significant change discovered in the CNCS results. It is feasible that the DPD jump frequencies could be extracted using the model described by Gapontsev et al., but this method also does not correlate directly to the concept of a stretched exponential or what is implied by the $<\tau>$ or $\beta_{KWW}$ values obtained from the fits here. As is mentioned earlier, a Gaussian jump diffusion analysis is used elsewhere for ISF analysis, but this is more typical of a confined liquid and may not be an accurate description of the expected diffusive modes within a deformed PdH$_x$ sample. The isotropic Chudley-Elliot model is applied above for comparison purposes, but these are estimates as it would be expected there is a more applicable model. This work simply proposes that such a model can be used, and gives representative FWHM vs. Q plots that can be corroborated by ab initio examinations of the dislocation structure and its interaction with hydrogen, or an extension of the ab initio principles into a classical MD simulation. However, general trends from these results provide many details about the system. Dislocation theory relates that is an inverse relationship between the tensile strain and radius from dislocation core, and that strain will enhance the diffusive processes of small interstitial hydrogen. Since hydrogen detrapping occurs above 300K [76], the region between 150K and 300K has population that is temperature and [H] dependent. At the hydrogen concentrations sam-
pled here, it appears there is 1) reduced site blocking near dislocation, 2) more jumps occurring in strain-mediated solute diffusion region, 3) ease of transfer from trapping site into a core site, which then allows for greater percentage of “DPD jumps” that have their barriers lowered by the significant increase of lattice strain with the core. Essentially, the size of the Cottrell atmosphere likely dictates the KWW-exponential transition regime, which explains why a temperature and concentration driven process occurs. As discussed in Chapter 2, it has been proposed that hydrogen can reform a weak $H_2$ bond in deformed Pd and diffuse as a gaseous molecule, which could explain why a significantly depressed diffusion mechanism is seen even at 250K, below the temperature in which such jumps are expected. All of this assertions must be made with caution due to some concerns. Ignorance of the error during the Fourier transform could have led to uncharacteristically strong fits for every fit type tested, but it is assumed that modeling the variance at each point as contained within the data point itself properly accommodates this concern. Also, while general trends can be seen in the results for the secondary diffusive mode, the lack of an adequate energy transfer window makes it impossible to fully model the single exponential decay process in the stretched/single exponential fits. Finally, since it seems necessary to use an average $\beta_{KWW}$ in order to decrease the variability of $<\tau>$ and obtain results that correlate somewhat to the Chudley-Elliot model, the QT-dependence of $\beta_{KWW}$ may not yield as reliable of a description of the DPD diffusive modes as a simpler T-dependent description will.
Chapter 7

Conclusions

This work proposes the possibility of applying simultaneous QENS analysis for different instruments, and applies a known model for relaxation times of ISF in order to characterize the behavior. It also highlights material interactions up to and including the most recent work known in order to characterize the possible diffusive action within the deformed PdH$_x$ system. However, this paper does not reach any firm quantitative values that can identically relate to the proposed analytical models, instead using a qualitative description and a quantitative approximation to describe diffusivity for dislocation pipe diffusion. This work clarifies how to characterize the uniform background technique applied in the DAVE analysis [12], and confirms that the Chudley-Elliot model can be used as at least an approximation for the annealed PdH$_x$ system. Deformed PdH$_x$ samples have decreasing $\beta_{KWW}$ in Q, but in relationship to temperature are at their lowest at 300K. This could imply that there is more heterogeneous action happening at this temperature, which is in direct relation to the hydrogen detrapping transition occurring at 300K as indicated elsewhere [76]. It is obvious, though, that significant differences exist between the deformed and annealed sample sets. It is possible that a modification to Gapontsev’s model could be applied to see if the data is valid, but this verification is outside the scope of this work. The application of a simultaneous analysis of results from different QENS spectrometers was successful when the results were translated from $S_{inc}$ (Q,E) to $F_{inc}$ (Q,t), demonstrating that a range of diffusive modes can be modeled simultaneously when data is considered from instruments with different parameters. However, the limited resolution of the BASIS instrument and poor determination of data from HFBS limited the analysis of the slower, more bulk-like diffusive mode seen in the deformed samples at all temperatures tested. It is feasible to suggest that neutron spin echo spectroscopy could help extend the viable range for the data due to the significantly finer energy resolution possible using this method, on the order of neV. Using a better resolved method and combining the results with the well-resolved description of the DPD mode obtained here would ensure that a theoretical description could be made more viable.
References


[63] T.-N. Yang, Trapped Hydrogen Vibrational Density of States Measurement Using IINS PdH$_0.0011$ at 5K and 300K With Incident Neutron Energy of 250 meV. Master’s, University of Illinois at Urbana-Champaign, 2013.


Appendix A

Additional Figures

A.1 Experimental Methods

Figure A.1: Schematic of the BASIS instrument at ORNL, demonstrating the indirect geometry incurred by the use of backscattering Si(111) panels. From [99].

Figure A.2: Schematic of the CNCS instrument at ORNL, demonstrating the direct geometry of the instrument. The linear set of choppers works to modulate the neutrons to a narrow $E_i$ range, and the detector bank covers 1.7 steradians in order to provide information on a wide range of scattering angles. From [100].
A.2 Results

(a) $S_{inc}(Q, E)$ for B-Def-1 at 20K.
(b) $S_{inc}(Q, E)$ for B-Def-1 at 150K.
(c) $S_{inc}(Q, E)$ for B-Def-1 at 200K.
(d) $S_{inc}(Q, E)$ for B-Def-1 at 250K.
(e) $S_{inc}(Q, E)$ for B-Def-1 at 350K.
(f) $S_{inc}(Q, E)$ for B-Def-1 at 400K.
(g) $S_{inc}(Q, E)$ for B-Def-2 at 15K.
(h) $S_{inc}(Q, E)$ for B-Def-2 at 220K.
(i) $S_{inc}(Q, E)$ for B-Def-2 at 260K.

Figure A.3: $S_{inc}(Q, E)$ for all samples on BASIS. Energy transfer window is specified in meV for ease of comparison.
(j) $S_{inc}(Q, E)$ for B-Def-2 at 300K.

(k) $S_{inc}(Q, E)$ for B-Def-2 at 350K.

(l) $S_{inc}(Q, E)$ for B-Ann at 15K.

(m) $S_{inc}(Q, E)$ for B-Ann at 200K.

(n) $S_{inc}(Q, E)$ for B-Ann at 280K.

(o) $S_{inc}(Q, E)$ for B-Ann at 350K.

Figure A.3: (cont.) $S_{inc}(Q, E)$ for all samples on BASIS. Energy transfer window is specified in meV for ease of comparison.
Figure A.4: $S_{inc}(Q, E)$ for all samples on CNCS and HFBS. Energy transfer window is specified in meV for ease of comparison.
(j) $S_{inc}(Q, E)$ for C-Def at 10K, symmetric.

(k) $S_{inc}(Q, E)$ for C-Ann at 250K, symmetric.

(l) $S_{inc}(Q, E)$ for C-Ann at 295K, symmetric.

(m) $S_{inc}(Q, E)$ for H-Def at 5K.

(n) $S_{inc}(Q, E)$ for H-Def at 250K.

(o) $S_{inc}(Q, E)$ for H-Ann at 300K.

Figure A.4: (cont.) $S_{inc}(Q, E)$ for all samples on CNCS and HFBS. Energy transfer window is specified in meV for ease of comparison.
Figure A.5: Intermediate scattering function for BASIS, on log(t) scale. Due to the limited energy window, the valid data points are limited to those at $t > 90$ ps. As can be seen, essentially no attenuation of $F_{\text{inc}}(Q, t)$ happens in the B-Ann 250K sample, since it is below the hydrogen depopulation temperature of 300K. Also, the 350K B-Ann sample exhibits attenuation similar to that of the 350K B-Def-1 sample.
Figure A.6: No attenuation at all across the well-defined instruments at low annealed temperature range.
Figure A.7: MATLAB analysis of intermediate scattering function for combined data. Resolution cutoffs have been applied due to Q-dependent energy transfer window limits.