OPTICAL SPECTROSCOPY OF NANOSTRUCTURED MATERIALS

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OPTICAL SPECTROSCOPY OF NANOSTRUCTURED MATERIALS

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Dissertation

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ABSTRACT

Significant interest in nanotechnology is stimulated by the fact that materials exhibit qualitative changes of properties when their dimensions approach nanometer scales. Quantization of electronic, optical, and acoustic energies with nanoscale dimensions provides exciting, novel functions and opportunities, with interests spanning from electronics and photonics to biology. Characterizing the behavior of nanoscale materials is critical for the full utilization of such novel properties, but metrology for nanostructures is not yet well developed. In particular, mechanical properties of nanoscale particles or features are critical to the manipulation and stability of individual elements, yet changes in mechanical and thermodynamic properties in nanostructured materials create complications in fabrication. This thesis involves the application of Brillouin light scattering to quantify and utilize confinement induced vibrational spectra to understand phononics and elastic properties of nanostructured materials.

Measurement and proper interpretation of acoustic waves in polymeric, inorganic, and biological nanostructures provides information about elastic properties and self-assembly. Brillouin light scattering was used to study the vibrational spectra of two-dimensionally confined photoresist and silicon oxide nanolines and three-dimensionally confined poly(methyl methacrylate) spheres and spherical-like viruses. These applications extend the capabilities of Brillouin from characterization of thin films and well-defined spheres to more complex structures.
Acoustic waves propagating along the polymeric and silicon oxide lines allowed determination of modulus and its anisotropy. An unexpected acoustic mode was identified in the spectra from nanolines that provided a means to measure mechanical anisotropy. In polymeric lines as narrow as 88nm, neither a change in elastic properties relative to bulk elastic values nor anisotropy in elastic constants was observed. The acoustic waves propagating within polymeric and silicon oxide nanolines were mostly similar, but differed somewhat due to the ratio of elasticities between the lines and the substrate. More localized vibrations were observed in the photoresist lines than in the silicon oxide lines, both of which rested on a silicon oxide substrate.

Analysis of the Brillouin spectra from *Wiseana* Iridoviruses (WIV) revealed strong mechanical coupling between close-packed viruses, unlike the behavior of polymeric colloidal particles. In contrast to traditional model assumptions, Brillouin spectra indicated that their DNA core, rather than their protein shell, dominated the elastic properties of WIV.
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CHAPTER I

INTRODUCTION

Polymers are increasingly finding specialized applications in which the structures of polymers on the molecular or nanometer scales create novel or improved materials properties. In fact, a recent explosion of nanotechnology has taken place across materials science, spanning from biomedical to microelectronics and photonics applications. The enthusiasm for nanotechnology springs from the potential offered by qualitatively unique properties when the dimensions of a particle are comparable to some intrinsic length scale of the material. New opportunities for engineering at the nanoscale arise from these size-dependent optical, electronic, magnetic, or mechanical properties.\textsuperscript{1,2}

In metallic and semiconducting particles, nanoscale dimensions induce quantum confinement and changes in the density of electronic states. Quantum dots (QDs) are a typical example of materials that exhibit novel size dependent properties, namely electronic and optical.\textsuperscript{3,4} In QDs, the radii of semiconductor spheres or of core-shell nanoparticles are comparable to the exciton radius (~2-10 nm), or the distance between unbound electrons and holes, that combine to emit a photon. The energy of the emitted photon, or color emitted by the QDs, is directly related to the size of the particle. Metallic nanoparticles (~5-100 nm) exhibit a phenomenon known as surface plasmon resonance (SPR), in which conduction band electrons oscillate collectively within the
boundaries of the particle. Induced by visible light, SPR introduces incredible possibilities ranging from single molecule spectroscopy to cancer treatment.

Just as quantum confinement introduces novel properties in semiconductors and metals, molecular or chain confinement can induce qualitative changes in small molecule and polymeric glass formers. Many properties subject to so-called “finite-size” and chain confinement effects have been studied, from mass density and thermal expansion to surface dynamics, glass transition temperature, and mechanical properties. In most polymers, a characteristic length scale is the diameter of a chain molecule, with typical random coil end-to-end radius in the range of ~5-50 nm. Thus, it can be expected, and indeed observed, that qualitative property changes appear in polymeric structures not from quantum confinement, but due to chain confinement effects in structures as large as 50-100 nm.

Polymer thin films are interesting systems to study because the thickness, the one dimension of nanoscale confinement, can be made comparable to single molecular dimensions. From a practical standpoint, the one-dimensional confinement of thin films should be the simplest nanostructure to study. However, surface and interface effects dominate nanoscale materials, complicating the picture for studies of glass transition temperature and molecular dynamics of thin films. No comprehensive ideas exist for the behavior of the glass transition temperature of polymer thin films, a field where decreases, increases, and no changes have been observed for films confined below molecular dimensions.

Currently there is a lack of reliable metrologies that can quantify mechanical properties in soft-matter nanostructures. The few techniques that exist for mechanical
measurements of more rigid nanoscale materials indicate deviation from bulk behavior for a wide variety of material compositions. Here still, Young’s modulus, for example, has been found to increase, decrease, or remain constant in nanoscale materials depending on size and shape of the solid. The number of variables affecting the behavior of materials at the nanoscale creates a strong demand for reliable metrologies to quantify mechanical properties.

This dissertation focuses on applying optical spectroscopy to quantify vibrational and mechanical properties of nanostructures. Although wavelengths lie in the range of 400-700 nm, visible light is used to probe materials with sub-100 nm dimensions. Optical spectroscopy avoids the complications of and improves upon techniques that require physical manipulation of nanoscale materials or the use of short wavelength energies.

Chapter II reviews studies and discusses the current understanding of materials behavior in polymer nanostructures, focusing on the widely studied glass transition temperature and mechanical properties. Structures used in lithography processing as well as biologically inspired (virus-based) technologies provide motivation for developing new metrologies such as Brillouin light scattering, which is described in detail for its applications to thin films, lines, and spheres.

Chapter III introduces the experimental technique and samples used in this work. These include instrumentation and settings for Brillouin light scattering from polymeric, inorganic, and biological nanostructures.

In Chapter IV, the utility of Brillouin spectroscopy is extended from thin films to polymeric nanolines and polymer spheres. Propagating and non-propagating vibrations
are observed that provide a means to monitor modulus in more than one dimension of confinement.

In Chapter V, the phononics of silicon oxide gratings are studied and compared to the vibrational behavior of polymeric structures on silicon oxide. Differences resulting from boundary conditions provide guidance for analyzing Brillouin spectra from future generations of polymeric nanolines.

Finally, Chapter VI describes the use of Brillouin light scattering to measure the mechanical properties of individual spherical viruses and their assemblies. The findings and analysis will be applicable to the growing number of self-assembly techniques involving monodisperse, symmetrical viruses and other biological nanomaterials.
CHAPTER II

HISTORICAL PERSPECTIVE

In recent decades, with emphases in microelectronics fabrication and the field of photonics, polymers have played integral roles in advanced materials fabrication in which feature sizes are equal to or much less than the wavelength of visible light. The emerging fields of nanotechnology and photonics are largely predicated on the ability to construct mechanical, electrical, and optical devices with sub-micrometer dimensions. Whether these devices are comprised of polymers, ceramics, or metals, it is common that polymers are used in the fabrication or templating process. Typical techniques include deep ultraviolet (UV) lithography, imprint lithography, or molecular self-assembly. However, working with materials at sub-micrometer length scales can be a challenge since many material properties deviate from their bulk-like behavior when confined to small structures or geometries. For example, thin film properties deviate from bulk values, including glass transition temperature ($T_g$), physical aging, modulus, compliance, and diffusion coefficients.

Novel applications for polymers at the nanoscale require reliable characterization of materials properties in nanostructures, for both fundamental understanding and technological advancement. At the fundamental level, the variety of findings for size-dependent glass transition temperature are leading to stimulating discussions,
experiments, and theories regarding confinement, molecular dynamics, and the glass transition phenomenon. On the practical side, nanostructures fabricated in the semiconductor industry demand a reliable technique to characterize mechanical properties, as pattern collapse continues to hinder miniaturization. New bio-inspired technologies are investigating the use of biological macromolecules (DNA, RNA, proteins, etc.) and biological complexes (e.g. viruses) for self assembling templates. These are just a few examples of the astounding growth in nanotechnology that truly does and will rely on the ability to characterize materials properties at the level of single nanoscale assembly units.

This chapter begins by exploring current capabilities to measure and understand deviations from bulk properties in one dimensionally confined nanomaterials, thin films. The glass transition temperature of polymeric thin films has been heavily studied, and these results will be reviewed to provide insight to size-dependent properties. Next, this chapter contains a critical analysis of currently available techniques to measure mechanical properties of thin films and their potential to measure structures with two and three-dimensional confinement, especially for photoresist patterns and biological structures. Specifically, section 2.2 will discuss bio-inspired technologies and the importance of mechanical properties of the biological (viral) components. Finally, the theory and application of the vibrational spectroscopy used in this work, Brillouin spectroscopy, will be described in Section 2.3. The goal of this chapter is to review the range of observations for size-dependent properties in polymers and lay the groundwork for extending optical spectroscopy from characterizing thin films to more complex polymeric, inorganic, and biological nanostructures.
2.1 Effects of Nanoscale Confinement on Polymer Properties

Significant challenges exist for understanding how polymers behave when confined to dimensions near their own equilibrium length scale. From a theoretical perspective, surface and interface effects start to dominate bulk properties in high surface area nanostructures. Experimentally, it is difficult to probe such quantities as glass transition temperature or mechanical moduli of features with molecular level size scales. Many studies have focused on size-dependent $T_g$ in polymer thin films, but the field is still phenomenologically driven. Quantifying $T_g$ in structures with higher dimensions of confinement are very scarce, but also indicate a deviation from bulk $T_g$.\textsuperscript{20}

In a review titled, “Effects of confinement on material behavior at the nanometer size scale,” Alcoutlabi and McKenna discussed thermodynamic, dynamic, and mechanical studies of polymer thin films.\textsuperscript{11} Focusing on observations of a size-dependent glass transition temperature, they summarized their findings in the following:\textsuperscript{11}

What is currently lacking is an overall view, which accounts for the range of observations. The field (of $T_g$ in ultrathin films) seems to be experimentally and empirically driven rather than responding to major theoretical developments.

This statement emphasizes two points i) the recognition of wide-ranging observations, which resulted from multiple experimental variables, and ii) polymeric behavior is not totally understood in nanoscale objects, where the feature dimensions are comparable to molecular dimensions. Both points attest to the importance of reliable metrologies for nanoscale materials, partly for developing theories of polymer behavior in nanostructures.

In addition to $T_g$, characterizing mechanical properties is especially difficult. Mechanical properties become particularly important for processing, design, and
application of microelectronic devices and micro- and nano-electromechanical systems (MEMS and NEMS). Nanoindentation or other scanning probe/force microscopy attempts to quantify hardness by applying a point-source force are complicated due to coupling of mechanical properties to the sampling volume, tip-sample interactions, and rate of energy dissipation. Further, for polymers, viscoelasticity, viscoplasticity, and blunt probes create difficulties for data interpretation. Simulations have provided some insight into moduli of materials nearing molecular dimensions. Still, few experimental techniques exist that reliably quantify elastic moduli of nanoscopic thin films and especially more complex structures.

In a discussion about characterizing polymer properties at the nanoscale, it is pertinent to comment on the current understanding of \( T_g \). This chapter begins by reviewing the current understanding of the \( T_g \) of thin films and continues into the mechanical behavior of polymeric nanostructures, from thin films to more complex features including viruses. The capabilities and advantages of optical spectroscopy for measuring mechanical properties of both synthetic and biological macromolecular nanostructures will be discussed. Specifically, Section 2.3 highlights the potential of vibrational spectroscopy to quantify high frequency mechanical moduli using acoustic vibrations in nanostructures.

2.1.1 One-dimensionally Confined Nanostructures: Thin Films

The emphasis on \( T_g \) studies in thin films is indicative of the effort dedicated to understanding materials phenomenon at the nanoscale. These findings have stirred
interest in thin film dynamics, mechanical properties, and other potentially size-dependent polymer properties.

2.1.1.1 Glass Transition Temperature ($T_g$)

The prime example of a dimension dependent macroscopic property is the glass transition temperature $T_g$ of a polymer. $T_g$ is an important macroscopic parameter that reflects thermodynamics and molecular dynamics of glass formers. Polymeric behavior, including mechanical properties, is strongly dependent on temperature relative to $T_g$. Multiple studies of various supported and free-standing films indicate appreciable $T_g$ shifts when the film thickness approaches 100 nm or less.\textsuperscript{25,26,27,28,29,30,31,32,33,34,35} The magnitude and direction of changes in $T_g$ vary based on sample preparation methods, substrate interactions, and measurement techniques.\textsuperscript{11} Empirical relationships exist for polystyrene (PS) thin films, as it is the most widely studied polymer thin film system exhibiting a $T_g$ dependence on film thickness.\textsuperscript{8} Despite abundant studies, however, descriptions of thin film behavior remain phenomenological, lacking a coherent theoretical model to describe the range of experimental results. Desire for fundamental understanding of molecular behavior in ultra-thin films and at surfaces and interfaces continues to drive many studies of polymer behavior at the nanoscale.

Forrest and Dalnoki-Veress in 2001 reviewed the topic of glass transition of ultrathin films.\textsuperscript{8} They reviewed experimental studies of glass transition temperatures in supported and unsupported (free-standing) films, as well as models that attempt to describe anomalies observed in the $T_g$ data. Studies of $T_g$ in thin films are rich with
potential extensions to surface and interface dynamics and length scales of cooperative
motion and glass transition dynamics. The following studies have led to models
suggesting dynamic heterogeneities\textsuperscript{36} and a molecular “sliding model” proposed by de
Gennes.\textsuperscript{37}

Forrest and Dalnoki-Veress’s review compiled the results from a variety of
techniques used to measure the glass transition temperature of supported polymer films,
with a compilation of experimental data for supported PS films shown in Figure 1. The
consensus among these studies was that the $T_g$ of supported thin films decreased from
bulk $T_{g}^{\text{bulk}}$ for film thicknesses less than $\sim 40$ nm, independent of molecular weight and
therefore polymer chain dimensions. The exception seemed to be an increase in $T_g$ for
films supported on substrates with attractive interactions between the film and substrate,
represented by the triangles in Figure 1.

![Figure 1](image)

Figure 1  Measured glass transition temperatures for a variety of supported PS thin films
and experimental techniques (Reprinted from Ref. 8 “The glass transition in thin polymer
films” with permission from Elsevier).
The commonly observed trend in Figure 1 was first observed for PS supported on hydrogen passivated silicon (Si) wafers,\textsuperscript{25} where the authors described the thickness dependent $T_g$ with the empirical relationship

$$T_g = T_g^{\text{bulk}} \left[ 1 - \left( \frac{a}{h} \right)^\delta \right]$$  \hspace{1cm} (2.1)

where $h$ is film thickness, and $a$ and $\delta$ are scaling parameters. Similar behavior has been observed for poly(methyl methacrylate) (PMMA) films on hydrophobic glass substrates,\textsuperscript{30} as well as polycarbonate,\textsuperscript{31} poly($\alpha$-methyl styrene), and polysulfone.\textsuperscript{32} Several techniques, including ellipsometry,\textsuperscript{33} positron annihilation,\textsuperscript{34} and dielectric spectroscopy\textsuperscript{35} validated thin film $T_g$ values reduced from the bulk value.

However, in systems where interactions between the film and substrate were strongly attractive, $T_g$ was found to remain constant or increase relative to bulk $T_g$ values, as seen by the triangles in Figure 1. Some examples include grafted films\textsuperscript{38} and poly-2-vinylpyridine\textsuperscript{39} or PMMA on oxide-coated Si.\textsuperscript{40} Whereas the $T_g$ of PMMA films on Au-coated glass substrates was found to decrease with decreasing film thickness, $T_g$ increased for the same thin films on oxide-coated Si.\textsuperscript{40} One can speculate that the reduced mobility at the substrate interface dominates the mobility of the entire film (or at least most of it) and causes an increase in $T_g$. Grohens \textit{et al.} observed a strong dependence on tacticity for the sign and magnitude of $T_g$ deviations from bulk values of PMMA films on hydrophilic Si wafers when measured using ellipsometry.\textsuperscript{41} They note that the reduced $T_g$ of syndiotactic PMMA ($s$-PMMA) and the increased $T_g$ of isotactic PMMA ($i$-PMMA) approaches the $T_g$ of bulk amorphous PMMA ($a$-PMMA) for the thinnest films measured (~20 nm). Also, as seen in Figure 2, they compare their results
to other dielectric studies. Both measurement techniques qualitatively indicated a decrease in $T_g$ for $s$-PMMA films of decreasing thickness, but opposite signs of $T_g$ change were observed for $i$-PMMA. The authors do not offer an explanation, but the qualitative difference may result from different surface conditions, namely aluminum electrodes were used for dielectric studies. Note, however, that interfacial interactions did not affect the qualitative behavior of $s$-PMMA.

Figure 2. $T_g$ (°C) as a function of film thickness for PMMA thin films on hydrophilic Si measured by ellipsometry and PMMA on aluminum measured by dielectric spectroscopy (Reprinted figure with permission from Ref. 41. Copyright 2002 by EDP Sciences).

The authors note that during ellipsometry measurements the glass expansivity remains constant while the melt expansivity decreases with decreasing film thickness, leading to a decrease in contrast, a phenomenon common for determinations of $T_g$ in all thin film studies.

Substrate effects can be eliminated by studying unsupported, or free-standing, films with two air interfaces. Forrest et al. studied the effect of free surfaces on the glass transition of unsupported PS films. They observed several remarkable trends for
unsupported films that deviated from supported film behavior. First, the qualitative
dependence of $T_g$ on film thickness differs from that of supported films. Reduced $T_g$
values in high $M_w$ unsupported films reduced linearly with decreasing film thickness, in
contrast to the widely observed behavior for supported films (Figure 1, equation 2.1).
Second, $T_g$ reductions were observed for unsupported films with thicknesses below ~70
nm compared to ~40 nm in supported films. Third, unsupported films exhibited $T_g$
reductions far greater in magnitude than those found for supported films. For example,
the $T_g$ of a 20 nm PS film reduced by 70 K when unsupported and only 10 K when
supported on a hydrogen-passivated Si wafer, as seen in Figure 3.28

![Figure 3](image_url)

Figure 3  $T_g$ of free-standing (triangles) and supported (squares, circles) PS thin films
(Reprinted figure with permission from Ref 28. Copyright 1997 by the American
Physical Society).

Additionally, studies of free-standing films emphasized the importance of chain
confinement effects for high molecular weight ($M_w$) unsupported PS films.28 Whereas $T_g$
reductions did not depend on $M_w$ for supported films, unsupported films showed a strong
dependence on $M_w$. However, unsupported PS films with $M_w \leq 378$ kg/mol exhibited the
same thickness dependent $T_g$ as supported films (equation 2.1). Thus, the behavior of $T_g$ of unsupported films as a function of film thickness fell into two $M_w$ regimes, depicted in Figure 4.

![Figure 4](image)

Figure 4 $T_g$ dependence on $M_w$ for unsupported films (Reprinted from Ref. 8 “The glass transition in thin polymer films,” with permission from Elsevier.). Low $M_w$ polymers behave like supported films whereas $T_g$ decreases linearly with thickness for high molecular weight polymer films.

Forrest et al. attributed reduced $T_g$ of unsupported films to finite-size effects correlated to the size of the cooperatively rearranging region ($\xi_{CRR}$) for PS of $M_w < 514$ kg/mol whereas polymer chain confinement effects dominated the behavior of higher $M_w$. Further, the high $M_w$ lines and the tangents to the low $M_w$ behavior in Figure 4 can be extrapolated to a point ($h^*, T_g^*$) that leads to an expression for $T_g$ reductions in terms of film thickness and molecular weight dependence. Low $M_w$ unsupported films behaved similarly to supported films in which weak polymer-substrate interactions resulted in a reduced $T_g$ compared to bulk $T_g$. Compare this to supported films in which
polymer-substrate interactions were the dominant factor in determining $T_g$ and led to an increase in $T_g$.\(^{28}\)

The molecular weight dependence and surface and interface effects of $T_g$ changes in thin films leads to interesting consequences for behavior of polymers in confinement. Several models have been proposed to explain the measurements of $T_g$ dependence on film thickness.\(^8\) The basic ideas include regions of increased mobility near free surfaces and decreased mobility near attractive substrates. One explanation is the so-called layer model, in which two to three layers with different rates of relaxation exist within the film cross-section.\(^{44}\) Another explanation is the sliding model proposed by de Gennes.\(^{37}\) In the sliding model, the sliding motion of chains, in competition with segmental mobility, dominates the chain mobility in thin films because the free surfaces allow chain ends to slide uninhibited, in contrast to the bulk. The sliding model predicts a linear dependence of $T_g$ on film thickness for high $M_w$ free-standing films, but does not explain the $M_w$ dependence or the convergence of the extrapolated data at $(h^*, T_g^*)$.\(^8\)

Studies of free-standing films have brought emphasis to the length scales at which chain confinement effects become important in high $M_w$ polymers and to the length scales involved in low $M_w$ glass formers. A number of experiments have concentrated on identifying specific length scales and dynamics at the surface, although without a conclusive experimental consensus. Some of the techniques used to investigate surface mobility in thin films include second harmonic generation,\(^{45}\) quartz crystal microbalance,\(^{46}\) relaxation of birefringence,\(^{47}\) dielectric spectroscopy,\(^{35,48}\) surface positron annihilation,\(^{49,50}\) near-edge X-ray absorption fine structure (NEXAFS),\(^{51}\) and atomic force microscopy.\(^{52}\) In general, relaxation functions of surface dynamics broaden rather than
shift to a lower temperature, and direct measurements of relaxation have observed both enhanced\textsuperscript{49,52} and bulk-like\textsuperscript{50} surface dynamics.

Simulations indicate an increased rate of conformational transitions that decay with a characteristic length from the surface into the bulk.\textsuperscript{53} In addition to observing a fluid-like interfacial layer where chain mobility was significantly higher than in the bulk of the film, simulations by Jain and de Pablo yielded $T_g$ reductions in unsupported polymer thin films that followed the empirical relationship in equation 2.1.\textsuperscript{54}

More recent experiments by the group of Torkelson have provided significant insight into the length scale and interfacial effects on $T_g$ of polymer thin films.\textsuperscript{55,56,57} In their ensemble fluorescence experiments, $T_g$ was identified by a change in the temperature dependence of a fluorescent label or chromophore dye intensity. Increases in local density of the nanoscale environment surrounding the chromophore decreases nonradiative decay and increases fluorescence intensity. The temperature dependence of fluorescence intensity is stronger in the rubbery state than in the glassy state, leading to a kink in the intensity as a function of temperature.\textsuperscript{55} As in previous studies, the fluorescence ensemble studies revealed a reduction of $T_g$ in supported PS films, as in Figure 5, as well as a weakening in strength of the glass transition.\textsuperscript{57} Recall that contrast for determining $T_g$ by ellipsometry also decreased with film thickness.\textsuperscript{43}
This fluorescence technique made it possible to study $T_g$ of multilayered thin films with various film thicknesses and interfaces (as in Figure 6). They found a gradient of reduced $T_g$ values, with maximum deviations from bulk $T_g$ occurring at film-air surfaces. Further, the magnitude of reduced $T_g$ is dependent on overall film thickness, or more specifically, the proximity of a layer to a free surface or fixed interface. For example, a 12 nm PS surface layer coated onto another 12 nm PS layer exhibited a reduced $T_g$ of 11 K, whereas when coated onto a 24 nm PS layer it showed a reduced $T_g$ of 14 K. More dramatically, they found a reduced $T_g$ of 32 K for a 14 nm PS film coated onto a 270 nm PS layer. The substrates in these cases were glass slides, initially rinsed in 10% sodium hydroxide/70% ethanol/20% water solution then rinsed with solvent (toluene) between experiments.
Ellison et al. also measured the size of cooperatively rearranging regions, $\xi_{CRR}$, in bulk polymers, but did not find a correlation between the $\xi_{CRR}$ and the $T_g$-nanoconfinement effects. From these ensemble fluorescence measurements, the authors emphasize a continuous distribution of reduced $T_g$ from the surface, rather than two or three distinct layers as predicted by models describing increased surface dynamics.

As reviewed above, extensive studies have been performed and models have been developed in attempts to find universality and a first principles explanation for confinement-induced behavioral change in $T_g$ polymer thin films. The above discussion is merely a sampling of the studies of thin film $T_g$, which have yielded a qualitative understanding that deviations from bulk behavior take place in polymer nanostructures with feature sizes below ~40-70 nm. Surface dynamics may be faster than in the bulk and polymer chain length can strongly effect $T_g$ of thin films. Still, the field of size-dependent $T_g$ remains highly controversial due to the contradictory results and a lack of clear theoretical concepts.
2.1.1.2 Mechanical Properties

In contrast to thin film $T_g$, surprisingly few studies have concentrated on mechanical properties of thin films, partly due to the complexity of experimental techniques to mechanically manipulate and test nanostructures. $T_g$ reductions alone provide motivation to investigate possible changes in elastic constants, including intrinsic length scales for which finite size or chain confinement effects cause softening or stiffening. Technological applications such as microelectronics fabrication, MEMS, and NEMS require mechanical properties information for successful processing, design, and application for nanoscale polymers.

It seems most natural to apply direct force measurements to quantify mechanical properties of nanoscale structures. Typical techniques involve scanning probe microscopy tips and include nanoindentation,\textsuperscript{22,59} lateral force microscopy,\textsuperscript{60} dynamic atomic force microscopy (AFM),\textsuperscript{61} frictional force microscopy (FFM),\textsuperscript{62} and interfacial force microscopy (IFM).\textsuperscript{63,64} Nanoindentation may be one of the most popular techniques to measure hardness of materials, often based on work by Oliver and Pharr.\textsuperscript{65} Analysis of indentation data involves relationships derived for penetration of a particular shape into a flat elastic surface. The general relationship between penetration depth, $h_p$, and load, $P$, for indenter geometries follows as

$$P = \alpha (h_p - h_{p,f})^m$$  \hspace{1cm} (2.2)

where $\alpha$ represents the geometric constants, elastic moduli, and Poisson’s ratios of the sample and indenter, $h_{p,f}$ is the final unloading depth, and $m$ is a power law exponent.
related to the geometry of the indenter. Oliver and Pharr made two significant realizations and subsequently developed i) correction factors for the constantly changing slope of the unloading curve due to constantly changing contact area and ii) an expression for contact stiffness defined as the derivative of penetration with respect to penetration depth at the maximum loading point, \((h_{p,\text{max}}, P_{\text{max}})\).

\[
S^* = \left( \frac{dP}{dh} \right)_{(h_{p,\text{max}}, P_{\text{max}})} = \alpha n(h_{p,\text{max}} - h_{p,f})^{n-1}
\] (2.3)

The total system stiffness, \(S^*\), is the slope of the tangent to the unloading curve at \((h_{p,\text{max}}, P_{\text{max}})\) (Figure 7).

![Diagram of loading and unloading force curves](image)

Figure 7  Loading and unloading force curves obtained during a nanoindentation experiment and important parameters for analysis. (Reprinted with permission from Ref. 22, “Nanoindentation of Polymers: An Overview.” Copyright 2001 Wiley-VCH Verlag GmbH & Co. KGaA.)

Corrective factors to equation 2.2 require calibration of tip shape and load-frame compliance \(C_f\) for each tip-sample combination. The tip shape, shown schematically as a
cross-section in Figure 8, determines the contact area, which is critical for calculating modulus from indentation data. The compliance of the load-frame is subtracted from the total compliance to yield the sample compliance. One calibration technique is to use AFM imaging of a highly plastic reference material such as aluminum or fused silica. Another calibration technique is to assume that Young’s modulus, \( E \), and hardness, \( H = \frac{P_{\text{max}}}{A} \), of the sample are independent of penetration depth. In this method, \( C_f \) is determined from the y-intercept of \( C_{\text{total}} \) as a function of \( 1/(P_{\text{max}}^{1/2}) \).  

Figure 8  Cross-section of a conical nanoindentation at maximum load in a compliant surface. (Reprinted with permission from Ref. 22, “Nanoindentation of Polymers: An Overview.” Copyright 2001 Wiley-VCH Verlag GmbH & Co. KGaA.).

In a nanoindentation measurement, the force response of the sample to the indenter is measured. The spring constant of the sample can be obtained in the linear response regime. With proper calibration, stiffness and contact area, \( A \), can be used to calculate \( E \). However, a great number of uncertainties limit the reproducibility of calibration results and thus reliability of nanoindentation for determining modulus. Additional uncertainties exist beyond the main factors associated with determinations of load-frame compliance and tip-shape. Namely, detection of a true zero in load and displacement, load and displacement measurements themselves, elasticities of the sample
and indenter materials, and correction factors for material pile-up or sink-in around the tip-sample contact all complicate interpretation of indentation data.\textsuperscript{22}

Other issues preclude the use of nanoindentation and other probe-based metrologies for nanoscopic features. First, the apex diameters of mechanically robust tips are typically greater than 20-50 nm. Also, mechanical coupling to the sample volume,\textsuperscript{64} tip-sample interactions, and the rate of energy dissipation\textsuperscript{59,61} further complicate the interpretation of the data for features confined to sub-100nm scales in two and three dimensions. Applying nanoindentation to polymer films has not resulted in correct estimates of modulus values, often leading to higher (at least 15\% greater) than bulk values and potentially artificial moduli decreases with penetration depth.\textsuperscript{22,23} Instrumental limitations such as load resolution of $\pm 100$ nN and the inability of most instruments to detect initial contact loads less than 1 $\mu$N create specific difficulties when applying nanoindentation to polymers, especially if $E < 1$ GPa or the indents should be less than 1 $\mu$m.\textsuperscript{22} Because traditional analysis relies on a linear elastic response from the material, viscoelastic polymer properties such as creep and pile-up require more complete theoretical models to extract meaningful modulus data for polymer films.\textsuperscript{22,23} Non-linear force response from thin elastic shells will be discussed further in section 2.2.2.

A modification of beam bending, wafer curvature has been developed to simultaneously quantify Young’s modulus, Poisson’s ratio, and the coefficient of thermal expansion of dielectric thin films.\textsuperscript{66} Curvature testing based on temperature variation of bilayer structures has yielded similar information,\textsuperscript{67} but has not provided insight to a length scale at which polymer properties deviate from the bulk.
Quartz crystal microbalance (QCM) technique can probe mechanical relaxation dynamics from ~4-100 MHz. QCM measures the shear viscoelastic response of a supported film from the change in frequencies and damping constants of the acoustic modes in the film. Application of QCM is unpractical for ultrathin films and more complex structures because the changes depend only on the mass at nanoscale thicknesses.

Vibrational techniques such as Brillouin light scattering and surface acoustic wave spectroscopy (SAWS), as well as new developments of differential ultrasonic force microscopy and atomic force acoustic microscopy (based on ultrasonic actuation with scanning probe microscopy (SPM)) are nondestructive techniques capable of probing elastic moduli. Although the latter two techniques have demonstrated successful nanoscale imaging of mechanical responses, interpreting raw data for meaningful elasticity information still requires intimate knowledge of SPM tip geometry, which should be frequently monitored using reference samples with known elastic constants.

Forrest et al. measured the mechanical properties of multi-layered PS and polyisoprene (PI) films using Brillouin light scattering. Brillouin probes acoustic wave velocities that are proportional to the square roots of elastic constants. The advantages of the multi-layered geometry included i) total film thickness large enough to eliminate substrate and/or free surface effects and ii) individual layers with only one type of interface. Individual layer thicknesses ranged from \( d \sim 16 \text{ nm} \) to \( d \sim 80 \text{ nm} \). They concluded that mechanical properties of polymers exhibit little or no change even when
the molecules were forced into highly confined geometries, with a dimension less than the unperturbed size of the polymer molecules, $R_{EE}$.

In free-standing films, Forrest et al. also used Brillouin light scattering to find that room-temperature moduli remained unchanged to within 1% for all films differing in $T_g$ by as much as 65 K from bulk $T_g$\textsuperscript{76}. Further, mechanical stiffness, mass density, and thermal expansion of thin, unsupported PS films in the glassy state were consistent with bulk values for all film thicknesses, as thin as 29 nm. The utility of this optical spectroscopy technique will be discussed in more detail in section 2.3.

SAWS uses plane-waves generated by a line-focused pulsed laser that are detected by an interferometer to measure phase velocity dispersions over hundreds of megahertz\textsuperscript{71,72}. SAWS has been used, for example, to determine thickness and Young’s modulus of titanium nitride films with thickness down to ~300 nm and Young’s modulus nearly 500 GPa\textsuperscript{72}. According to a 2004 report on nanometrology from the National Institute of Standards and Technology (NIST), sub-500 nm films were previously a challenge for SAWS, but properties were extracted from 50-100 nm stiff capping layers on specific substrates (compliant functional films)\textsuperscript{77}.

A recently developed technique has resulted in stimulating findings, indicating possible deviations of mechanical properties in supported polymer films with thicknesses comparable to about three molecular diameters\textsuperscript{15}. This technique relies on the elastic buckling instability of stiff films on a soft deformable substrate\textsuperscript{14,15}. Stafford et al. found a reduction in modulus from bulk values for PS and PMMA films with thicknesses below ~40 nm, as seen in Figure 9. Interestingly, they cannot account for the modulus reductions by applying a composite model with a soft surface layer of the film\textsuperscript{15}.
While particularly helpful as a high-throughput metrology for thin films, including hydrogels for biomedical applications,\textsuperscript{78} interpretation of buckling data for more complex structures remains a challenge.

Yoshimoto \textit{et al.} used coarse grain polymer modeling to calculate the dynamic mechanical properties of unsupported (free-standing) PS films.\textsuperscript{16} They found that mechanically soft layers develop near the free surfaces and increase in thickness until comparable to the entire film thickness near $T_g$. Thus, they observe a melt-like region at free surfaces and a glass-like region in the middle of the film.\textsuperscript{16}

So, very few experimental techniques provide reliable mechanical information about polymeric thin films, and simulations provide some guidance for the field. The challenge becomes greater for structures of higher confinement dimensionality.
2.1.2 Multiple Dimensions of Confinement: Photoresist Patterns

Extending the experimental techniques discussed above to quantify properties ($T_g$, modulus, or otherwise) of more complex soft-matter nanostructures is extremely challenging due to additional boundary conditions and in some cases reduced symmetry introduced by two or more nanoscale dimensions. Measurements of mechanical properties, in particular, are limited by the very few, if any experimental methods that can provide reliable information. The challenges facing metrologies discussed in the previous section for thin films, for example nanoindentation, other force microscopies, or the new buckling-based metrology, are amplified by the complexity of structures with additional confinement geometries and the fragile nature of nanostructures. To evaluate both characterization techniques and materials properties at the nanoscale, well-defined and practically useful nanostructures created in the microelectronics industry provide excellent model samples.

Deep UV lithography is routinely used in the semiconductor industry, to create nanostructures in polymeric photoresist films, examples of which are shown in Figure 10. The elastic modulus of these polymeric lines is of paramount importance for a wide range of emerging applications that span microelectronic, photonic, nano-electro-mechanical systems, nanofluidic, and biomedical technologies. However, as seen in thin films, polymers are susceptible to material property deviations ($T_g$, modulus) when the relatively large macromolecules, random coils with dimensions on the order of 5 to 50 nm, are confined to structures that approach these scales.
At the nanoscale, forces that are negligible in macroscopic systems, such as surface tension, often become significant. During the resist process, outlined in Figure 11, the material from the trenches is dissolved with an aqueous base and rinsed clean with deionized water.

Figure 11 Simplified schematic of resist processing. Collapse of the patterned lines occurs during the drying of the resist features. (Reprinted figure with permission from Ref. 83. Copyright 2000 American Vacuum Society.)
As the water dries from the structures, a liquid meniscus forms in the channels between the polymeric walls (Figure 11). The tight radius of curvature of this meniscus generates large Laplace pressures that tend to collapse the structures (Figure 12). In fact, pattern collapse increases significantly above a critical height to width aspect ratio of the structures (e.g. Figure 13), termed the critical aspect ratio of collapse (CARC). In the semiconductor industry where the minimum feature widths are now below 100 nm, this critical aspect ratio is approximately 3:1.

![Figure 12 Pattern collapse/failure (material failure, left; elastic or plastic deformation, right) of photoresist patterns resulting from the rinse process of lithographic processing (image courtesy of Chris Soles, NIST, 2003).](image)

![Figure 13 Percentage of Shipley Apex E photoresist patterns collapsed as a function of height to width aspect ratio, with 150 nm linewidth and 450 nm spacing, as estimated by scanning electron microscopy (Reprinted figure with permission from Ref. 83. Copyright 2000 American Vacuum Society.)](image)
Although estimates of CARC provide practical knowledge, it is difficult to estimate intrinsic mechanical moduli of the resist material. Perhaps the scale of confinement reduces modulus of the structures and their resistance to collapse.

Recent simulations suggest that Young’s modulus of lithographically patterned polymer nanostructures decreases and even becomes anisotropic when the feature size becomes comparable to a few (approximately 3) molecular diameters. Such a modulus reduction magnifies the instability of structures fabricated at these length scales and signifies a marked departure in the isotropic nature of amorphous polymers.

Specifically, the group of Juan J. dePablo performed Monte Carlo and molecular dynamics simulations to study the effect of confinement on mechanical properties of two-dimensionally confined structures. Their structures mimicked the rectangular polymeric lines formed in lithography and ranged in size from 36 to 1764 polymer chains. Lennard-Jones interaction potentials and harmonic springs were used between monomer units. They applied virtual deformations to measure compressive strain in the height direction, which are analogous to atomic force microscopy experiments and continuum-mechanics analyses of modulus ($E = \frac{\sigma}{\epsilon}$, where $E$ is Young’s modulus, $\sigma$ is stress, and $\epsilon$ is strain). Virtual deformations resulted in similar mechanical behavior as analysis from molecular level approaches of strain fluctuation and elastic bath calculations, affirming their assumption that the features follow continuum-like behavior. They note, however, that size-dependence of modulus requires a molecular level understanding.

Figure 14 shows the simulated decrease of Young’s modulus from the bulk value for line widths below $15-20\sigma$. 
According to their rough estimates, $\sigma \sim 2$ nm if correlated to the Kuhn segment length for a polymer like poly(methyl methacrylate), and their molecules have radius of gyration $\sim 3\sigma_{LJ}$. Correspondingly, they estimate a departure from bulk moduli for glassy polymer feature dimensions of $\sim 30$-$40$ nm. As a reference, for free-standing films with thickness of the smallest dimension $9\sigma$, where $\sigma$ is the length of a single Lennard-Jones potential interaction site estimated to be $\sim 2$ nm, the $T_g$ was only about 7% below that of the bulk. Figure 15 shows Young’s modulus as a percentage of the bulk value for different directions of the structures under varying dimensions of confinement. Whereas the modulus decreases to about one-third that of bulk in the height dimension, the modulus in the width dimension of these smallest structures is only $\sim 11\%$ of the bulk modulus.
Thus, Van Workum and de Pablo conclude that nanostructures lose their mechanical rigidity in the most highly confined dimensions. They attributed the decrease in modulus to higher mobility at surfaces and increased surface to volume ratios. These simulations, together with the increasing demand for smaller patterns, amplify the demand for direct measurements of elastic properties in polymeric nanolines for successful modeling and optimization of mechanical behavior.

Mechanical properties for new lithography techniques, such as nanoimprint or step-and-flash lithography, are critical to pattern stability, but changes in $T_g$ as observed for thin films also play a crucial role in pattern development. Until recently, experimental measurements of $T_g$ in nanoscale polymeric patterns were not possible. Torkelson’s group has extended their ensemble fluorescence technique from thin films to measurements of $T_g$ in rectangular polymeric nanolines.\textsuperscript{20} They investigated the $T_g$ of PMMA nanolines on silica, in comparison to films of identical thickness. They found $T_g$ to reduce more in the polymeric lines than in the films, with larger $T_g$ reductions resulting
from thinner features. Also, in agreement with the wealth of $T_g$ studies in thin films, attractive PMMA-silica interfacial interactions increased $T_g$ while free surfaces resulted in reduced $T_g$. Figure 16 shows how the presence of free surfaces on the nanolines led to a reduction of $T_g$ for an 18 nm film with a $T_g$ greater than bulk PMMA.

Figure 16  Difference of $T_g$ for PMMA lines and bulk PMMA as a function of line width, as measured by ensemble fluorescence, with various thicknesses, 175 nm (circles), 30 nm (triangles), 25 nm (+), 20 nm (diamonds), and 18 nm (squares). The horizontal dotted lines show the values of $T_g$ relative to bulk PMMA for thin films with corresponding thicknesses. (Reprinted with permission from Ref. 20. Copyright 2007 American Chemical Society.)

Simulations in the group of de Pablo and recent $T_g$ depressions of polymer nanolines found by Torkelson’s group increase the need for reliable experimental techniques to quantify mechanical properties of polymeric nanostructures.

2.2 Biological Nanostructures

In many ways, biology is the most complex natural science. Across the kingdom of life, miraculous traits exhibit themselves naturally, without modern “high-tech” intervention. These exceptional qualities arise from modifications, or evolution, of the
genetic codes in living organisms. The building blocks of life, deoxyribonucleic acid (DNA) molecules, are biological polymers of nucleotide monomers that hold the genetic codes, or blueprints of life. The recent human genome project provided and will provide deep insight into specific roles of DNA. Recently, a controversial theory received publicity in *Science* for its creativity and potential impact to modern evolution theory.\(^8^5\)

Patrick Forterre, an evolutionary biologist at the University of Paris-Sud in Orsay, France, suggests that essentially, evolution of all living species can be traced back to the genetic codes contained within viruses. The theory in its entirety is a subject for debate, but the role of viruses as genetic mutators, for example when infecting cells, is well-established.\(^8^6\)

Forterre’s theory, together with a perspective article in the same volume of *Science*,\(^8^7\) provide insight to the motivation behind bio-inspired virus-based technologies. Their importance as genetic delivery vessels alone inspires studies of their structural, physical, and chemical properties. Modern medicine can potentially harness empty viral capsids as drug delivery pods for specific gene therapy directed by the capsid chemistry.\(^8^8\) Each interface of a virus, the shell exterior, interior, and the core surface, offers a location for specific chemical functionalization.\(^8^9\) Recent studies have taken advantage of these interfaces to find new applications for next generation nano-electronic and optoelectronic devices.\(^8^7,8^9,9^0,9^1,9^2,9^3\)
2.2.1 New Frontiers for Viruses

Viruses are traditionally considered dangerous objects that are capable of hijacking cellular function and of mutating plant and animal genetic material for their own selfish reproductive purposes. New technologies, however, are finding ways to harness their amazing functionality. The packaging and release mechanisms of the capsid shells, as well as their monodispersity, shape, size and multivalent, site-specific surface functionality make them attractive for a broad array of technologies, ranging from targeted drug delivery and gene therapy, to templates for complex photonic and electronic materials.\textsuperscript{87,89,94,95,96}

For example, cylindrical viruses (tobacco mosaic virus, M13 bacteriophage) offer controlled, uniform anisotropy, an elusive characteristic for nanoparticles, and have been utilized as templates for metallic and semi-conducting nanowires and as scaffolds for nanoparticle arrays with potential as data storage devices,\textsuperscript{97} light-harvesting systems,\textsuperscript{98} and batteries.\textsuperscript{99,100} Juhl \textit{et al.} harnessed the nearly spherical Wiseana iridescent viruses (WIV) from infected larvae (Figure 17) and managed to assemble WIV in vitro into colloidal assemblies that exhibited properties of a photonic crystal.\textsuperscript{96}

The structures of many viruses are known through the use of X-ray crystallography and cryo-electron microscopy. However, the proper use of viruses for various technologies depends on a number of characteristics, including the mechanical properties of the building block and its assemblies. As a template for material synthesis, the mechanical properties ultimately determine the particle stability and durability, and thus define the useful process and performance window of these biological colloids and
Figure 17  Larvae of the greater maxmoth, *Galleria mellonella*, uninfected (right) and infected (left) with WIV. The close-packed structure of WIV in the cell cytoplasm (inset) causes the highly infected larva to display slight discoloration and very-faint iridescence (Reproduced with permission from Ref. 96, “Assembly of *Wiseana* Iridovirus: Viruses for Colloidal Photonic Crystals.” Copyright 2001 Wiley-VCH Verlag GmbH & Co. KGaA.).

their assemblies. Biologically, mechanical characteristics of viral capsids are thought to determine morphological changes that occur during cellular infection. Receptor binding or changes between extra and intracellular environments, such as pH, have been proposed to induce strain and thus conformational changes of the proteins comprising the capsid.\(^{86}\) These factors trigger viral dissolution and the release of the infectious genetic material.

As advances in nanotechnology lead to novel materials properties, a realm of nano-biotechnology is emerging, in which emphasis is being placed on surface interactions of biological nanostructures. Bio-inspired photonics, adhesion, drug delivery, etc will all depend on the mechanical stability of biological nanostructures. As with polymeric nanostructures, development of analytical methods is necessary for accurate testing of mechanical properties of biological nanostructures.
2.2.2 Mechanical Properties of Viruses

Despite their importance, the mechanical properties of viruses remain largely unexplored, mainly due to their extremely small sizes and complex core-shell structure. Experimental techniques such as nanoindentation,\textsuperscript{101,102,103} together with finite element analysis, have provided rough estimates of properties of individual viruses. Generally, the force response of the virus capsid to the indentation is measured. The spring constant can be directly obtained in the linear response regime. Young's moduli, $E$, of virus capsids have been estimated by comparing the experimentally measured spring constant with the theoretical one on a basis of elasticity model and finite-element analysis.

In particular, the Young's modulus of empty capsids (virus-like particles) of DNA-containing viruses have been estimated at $\sim 1.25$ GPa for murine minute virus (MVM)\textsuperscript{103} and $\sim 1.8$ GPa for \( \phi \)29 bacteriophage,\textsuperscript{101} while much lower moduli have been found for capsids of RNA-containing, cowpea chlorotic mottle virus (CCMV) 140-190 MPa.\textsuperscript{102} The value $E \sim 1$ GPa has been estimated for Murine Leukemia Virus.\textsuperscript{104} The increased toughness of the DNA-containing capsids, both filled and empty, as compared to their RNA-containing counterparts, is attributed to the need to withstand high internal pressures imposed by tightly packed DNA molecules.\textsuperscript{102,105}

The nanoindentation experiments of viruses were subject to the same analytical difficulties as polymer films discussed in section 2.1.1. Specific corrections for nonlinear elasticity of virus capsids was discussed in a later publication from some of the above authors, Gibbons and Klug.\textsuperscript{106} Gibbons and Klug emphasized the importance of geometrical parameters of the viral capsid and the nanoindenter. Specifically, they
included shell thickness and the nanoindenter (AFM tip) geometry as non-negligible parameters in their finite element modeling. Their results indicated about 2-3 times higher Young’s modulus values than initially reported for CCMV and $\phi^{29}$ capsid shells. Specifically, for $\phi^{29}$, their corrections increased the estimate of Young’s modulus from 1.8 GPa to 4.5 GPa.

Many virus capsids have a simple symmetric geometry. The above mentioned capsids (MVM, CCMV) and larger iridescent viruses (chilo (CIV), WIV) are icosahedral and can be approximated as a sphere. Model calculations for the eigenfrequencies of the complete viruses, including the genomic core, usually assume an overall rigidity comparable to benchmark proteins, such as crystalline lysozyme ($E \sim 2.7$ GPa), without regard for the genome-protein core-shell composition. In reality, double stranded DNA (ds-DNA) is more rigid than RNA, and its stiffening effect on viral moduli was observed in the above nanoindentation studies. RNA has similar rigidity to lysozyme, but DNA has a Young’s modulus at least three times higher than RNA or lysozyme. Therefore, calculations using lysozyme may be applicable to viruses containing RNA, but not necessarily those containing DNA.

Atomic force microscopy tips have also been used in a nanomanipulator to study properties of biological fibers, including tobacco mosaic virus (TMV). Others have experimentally estimated Young’s modulus of TMV rods from AFM and a bending method that utilizes forces of surface tension, but obtained a broad estimate of $E = 6 \pm 3$ GPa. In such experiments, estimates of moduli are as variable as the frictional forces between the virus and substrate.
Using the symmetry of viruses might also make possible the use of vibrational spectroscopy to measure the eigenfrequencies of the capsids. In this way, vibrational spectroscopy can be a very powerful tool to estimate mechanical properties of viruses, and specifics are described in Section 2.3.3.

2.3 Utilities of Brillouin Spectroscopy for Nanostructures

Visible light spectroscopies are useful tools for studying materials properties. For example, molecular dynamics, chemical composition, and acoustic mode velocities can be analyzed using light scattering. In bulk materials, spectroscopy techniques probe discrete energy levels within a continuous distribution of energies based on selection rules. Energy levels within nanostructured materials, in contrast, are quantized due to geometrical confinement. Material length scales on the order of the excitation wavelength induce novel electronic, optical, and phononic characteristics. Therefore, spectroscopy provides a logical means to study quantized energies of nanostructures. In particular, Brillouin light scattering yields inelastic frequency shifts of light energy scattered from thermally excited acoustic phonons with sub-micron wavelengths $\lambda_{ph}$. Structures with critical dimensions near or below $\lambda_{ph}$ will display a rich Brillouin spectrum of surface guided and breathing modes related to the elasticity of the structure.

Brillouin has proven effective for quantifying elastic properties in free-standing and supported films, and colloidal crystals. Unexpected Brillouin features have been observed in shallow silicon gratings and localized modes have been observed in photonic/phononic crystals, both of which provide insight to acoustic
mode propagation in and elasticity of patterned materials. These studies are discussed in Sections 2.3.4.1 and 2.3.4.2, but first it is necessary to review the relationships between acoustic waves measured by Brillouin and the elasticity of the scattering media. After reviewing the principles of Brillouin scattering theory in section 2.3.1, principles of Brillouin spectroscopy are addressed in sections 2.3.2 and 2.3.3 as well as how Brillouin has been applied to measure discrete vibrational spectra in materials with feature sizes comparable to and less than ~500 nm.

2.3.1 Brillouin Light Scattering Theory

Brillouin scattering can be understood as the inelastic scattering of incident energy by thermally excited elastic waves, or acoustic phonons, in a sample. It is often described as a scattering event following criteria for Bragg’s Law and the Doppler Effect. That is, the total momentum and energy between the incident energy and excitation (phonon), must be conserved in the scattering process.

Brillouin scattering occurs from acoustic waves propagating with wave vector $\mathbf{q}$ and frequency $\omega(q)$ through a medium. Incident light with wave vector $\mathbf{k}_i$ and frequency $\omega_i$ scatters from the modulated dielectric constant with scattered wave vector $\mathbf{k}_s$ and frequency $\omega_s$. Conservation of total wave vector (energy and momentum) in the scattering process leads to,

$$\mathbf{k}_s - \mathbf{k}_i = \pm \mathbf{q} \quad (2.4)$$

with the scalar relationship between acoustic phonon frequencies, and by energy conservation the difference between incident and scattered frequency of
\[ \pm \omega(q) = \omega_s - \omega_i \] (2.5)

where the plus sign refers to phonon absorption/annihilation (anti-Stokes) and the minus sign refers to phonon emission/creation (Stokes). In a classical understanding, equation 2.5 represents the Doppler shift of an incident wave diffracted by an elastic wave moving either in the direction of \( q \) or \(-q\). The inelastic Brillouin frequency shift \( \omega(q) \) from acoustic phonons is given by a linear dispersion relationship with the velocity of sound in the medium, or the velocity of phonon propagation, \( V \)

\[ \omega(q) = 2\pi V = Vq \] (2.6)

Neutron, X-ray, and visible light Brillouin scattering are possible. The wavelengths of neutron and X-ray Brillouin are much smaller (2-4 orders) than the wavelengths of visible light photons and are capable of measuring acoustic waves on length scales down to \( \sim 1 \) nm. Spectral resolution of neutron Brillouin is usually sufficient to estimate sound velocities, but low signal strength prevents its application to materials with nanoscale volumes. On the other hand, X-ray Brillouin improves upon neutron Brillouin signal statistics by \( \sim 10^4 \), but suffers in spectral resolution. Despite a ratio of spectral resolution to incident energy of \( \sim 10^{-7} \), the high energy of X-rays only allows spectral resolution of \( \sim 240 \) GHz (8 cm\(^{-1}\) or \( \sim 1 \) meV from \( \sim 10 \) keV source), making it difficult to study acoustic phonons with adequate accuracy.

The signal strength and spectral resolution of Brillouin light scattering (BLS) makes it a more viable candidate for measuring acoustic vibrations in nanostructures. Leon Brillouin first investigated the interaction between thermally excited acoustic excitations and light in the early twentieth century. Utilization of such an interaction for Brillouin light scattering (BLS) became popular with the advent of the laser and the
development of a high contrast spectrometer designed by J.R. Sandercock. Current BLS spectrometers are capable of measuring inelastically scattered light in the 1 GHz – 1 THz (~0.3-30 cm⁻¹) frequency range with spectral resolution ~0.01 GHz (0.003 cm⁻¹). Using incident light of ~500nm (2x10⁵ cm⁻¹), the ratio of spectral resolution to incident energy of BLS is ~10⁻⁶. BLS is sensitive to acoustic phonons with wavelengths ranging from less than ~100 nm to a few micrometers and localized vibrations in features with even smaller dimensions.

Incident and scattered light propagating in the scattering medium have the dispersion relationships \( \omega_i = (c/n)k_i \) and \( \omega_s = (c/n)k_s \), where \( n \) is the refractive index of the medium and \( c \) is the speed of light in vacuum (~3 x 10⁸ m/s). From equations 2.5 and 2.6, the expression

\[
\frac{|k_s| - |k_i|}{n|q|} = \frac{V}{c}
\]  

relates the change in absolute values between incident and scattered wave vectors to the phonon velocity. The energies of phonons measured in Brillouin light scattering, with frequency in the range \( \sim 10^8 - 10^{11} \) Hz, are on the order \( E_{\text{phonon}} = h\nu \sim 10^{-26} - 10^{-23} \) J. (Frequency is related to angular frequency by \( \nu = \omega/2\pi \).) Light photons with wavelength \( \lambda \sim 500 \) nm have energy \( E_{\text{photon}} = h\nu = hc/\lambda \sim 10^{-20} \) J. Thus, the ratio of energies between photon and phonon is on the order of at least \( 10^3 \), and \( ~10^5 \) for low frequency phonons considered here (1-30 GHz). This large difference in energies between the incident/scattered photons and the excitation phonon makes it reasonable to approximate \( |k_s| = |k_i| = 2\pi n/\lambda_o \), where \( \lambda_o \) is the incident laser wavelength in vacuum, leading to

\[
|q| = 2|k_s| \sin(q/2)
\]  

(2.8)
where $\phi$ is the angle between $k_s$ and $k_i$, as in Figure 18. The distribution of the phonon spectrum is continuous, but only those modes with $q$ equal to the scattering wave vector $Q$ are observed (analogous to Bragg scattering from crystalline planes).

$$Q = \frac{4\pi n}{\lambda} \sin \frac{\phi}{2} \quad (2.9)$$

![Figure 18](image_url)

Figure 18  Incident ($k_i$), scattered ($k_s$), and scattering ($Q$) wave vectors in a scattering process.

To understand Brillouin scattering as Bragg reflection of the incident light by the moving diffraction grating generated by the elastic wave phonon, equation 2.8 can be written in the form of Bragg’s Law,

$$\lambda = 2a \sin (\phi/2) \quad (2.10)$$

where $\lambda = \lambda_o / n$ is the wavelength of the incident photon in the medium ($\lambda_o$ in a vacuum).

The phonon wavelength $\lambda_{ph}$ is equal to the Bragg spacing $a$, leading to

$$a = \lambda_{ph} = \frac{2\pi}{|q|} = \frac{2\pi V}{\Delta \omega} = \frac{V}{\nu} \quad (2.11)$$

Rewriting equation 2.11 in terms of phonon velocity observed by the measured Brillouin frequency shift $\nu$ yields
\[ V = \frac{\omega}{Q} = \frac{2\pi v}{Q} \]  \hspace{1cm} (2.12)

or in terms of scattering angle

\[ V = \frac{\lambda_n \omega}{4 \pi n \sin(\phi/2)} = \frac{\lambda_n v}{2 n \sin(\phi/2)} \]  \hspace{1cm} (2.13)

Scattering occurs from longitudinal acoustic (LA) and transverse acoustic (TA) vibrations, appearing as peaks with approximately Lorentzian lineshape, as seen for a LA mode from polystyrene in Figure 19.

![Figure 19](image)

Figure 19  Example of LA modes in a Brillouin spectrum, in this case from bulk polystyrene, in a back scattering geometry \((\phi = 180^\circ)\). The central peak is the elastic scattering and the two peaks near 15 GHz are both inelastic Brillouin peaks from longitudinal acoustic vibrations.

The frequency dispersions of LA and TA modes in the bulk are linear with \(Q\) (Figure 20). The acoustic longitudinal \((V_L)\) and transverse \((V_T)\) sound velocities are related to longitudinal \((M)\) and shear \((G)\) moduli through the relationships

\[ V_L = \sqrt{\frac{M}{\rho}} \]  \hspace{1cm} (2.14)
\[ V_T = \frac{G}{\sqrt{\rho}} \]  \hspace{1cm} (2.15)

where \( \rho \) is the mass density.

Figure 20  a) Frequency and b) velocity dispersion relationships of LA and TA modes in a bulk material with \( V_T = 1.5 \text{ km/s} \) and \( V_L = 3 \text{ km/s} \).

Scattering from LA modes is polarized, meaning the polarization of incident light does not rotate upon scattering. Scattering from TA modes is depolarized, meaning the polarization of incident light does rotate upon scattering. Selection of scattering geometry and polarization determine the observable modes and relative intensities. The Brillouin spectrum of a bulk sample in backscattering geometry (\( \phi = \pi \)) shows a single longitudinal acoustic (LA) mode that appears at frequency:

\[ \frac{\omega}{2\pi} = v = \frac{2nV}{\lambda_o} \]  \hspace{1cm} (2.16)

The polarizations of incident and scattered light can help identify the nature of modes observed in Brillouin scattering. The notation for polarization conditions is as follows. Light polarized in the scattering plane is \( p \)-polarized; light polarized perpendicular to the scattering plane is \( s \)-polarized, and \( p-ps \) refers to collection of both polarizations. The first letter refers to the incident light polarization; the second letter
refers to the orientation of the analyzer that selects polarization for collected light, such as p-s polarization for depolarized scattering conditions (incident light p-polarized, scattered/analyzed light s-polarized). In the absence of an analyzer, the Brillouin spectra contain p-polarized and s-polarized waves. A polarization analyzer placed in the scattered light path selects Brillouin modes scattered from phonons with a particular polarization.

Measurements of thin films or nanostructures on a planar substrate with a defined surface plane x-y and surface normal in the z direction typically use backscattering geometry. The wavevector geometries for backscattering from surfaces are shown in Figure 21, for Stokes and anti-Stokes processes resulting from antiparallel phonon wave vectors q parallel to the surface. The resulting Q, is the projection of the scattering wave vector onto the surface, generally represented as $Q_{||}$. Here the scattering angle $\theta$ is defined as the angle between the surface normal and the incident wave vector. In contrast to the single LA mode observed for bulk media, many modes are observed in the spectra from thin films. The reason for the multiple modes in thin films is two-fold.

![Figure 21](image)

Figure 21 Schematic of surface scattering in backscattering geometry, showing incident ($k_i$) and scattered ($k_s$) wave vectors with frequency $\omega_i$ and $\omega_s$, respectively. (a) Stokes and (b) Anti-Stokes scattering from phonon wave vectors q with frequency $\omega(q)$ (Reprinted from Ref. 124, “Determination of the elastic properties of a barrier film on aluminium by Brillouin spectroscopy,” with permission from Elsevier.).
Figure 22 Observable Brillouin spectrum from a thin unsupported film. In this case, the spectrum corresponds to a 524 nm polystyrene film on silicon. The frequency shift of the LA from bulk polystyrene is represented by the dashed lines labeled $-\nu_o$ and $\nu_o$.

First, the spectrum of phonons with wave-vector perpendicular to the film surface becomes discrete (quantized) due to limitations in thickness $d$:

$$m\lambda_m = m\frac{V}{v_m} = 2d$$

(2.17)

Here $m$ is an integer number, $\lambda_m$ and $v_m$ are the wavelength and the frequency of the phonon. Second, the decrease of the scattering volume broadens the $Q$-selection rules by $\sin^2(x)/x^2$, where $x = \pi d/\lambda$.

Together these factors explain the presence of the LA mode ($\pm \nu_o$) splitting in the Brillouin spectrum of the thin films as seen in Figure 22. The multiple modes resulting from thin film confinement are so-called longitudinal guided modes (LGM). If the surface of the film is perpendicular to the incident light, the energy split between two neighboring LGM peaks $\Delta \nu$ provides an estimate of the sound velocity:
\[ \Delta \nu = \nu_m - \nu_m \approx \frac{V}{2d} \tag{2.18} \]

In addition to LGM modes, surface waves are prominent in the Brillouin spectra of thin films. The frequency of these surface acoustic waves (SAW) depends on the angle between the surface normal and the incident wavevector \( \theta \):\(^{128}\)

\[ \nu_{SAW} = \frac{VQ_\parallel}{2\pi} = \frac{V}{\lambda} \sin \theta \tag{2.19} \]

where \( V \) is the phase velocity of the surface wave. Alternatively, in terms of surface wave velocity \( V \),

\[ V = \frac{2\pi
u}{Q_\parallel} = \frac{\nu\lambda}{2\sin \theta} \tag{2.20} \]

Two mechanisms exist for Brillouin scattering from surfaces of transparent media: the ripple mechanism and elasto-optic coupling.\(^{69}\) Waves with displacements normal to the surface, in the plane known as the sagittal plane, create a corrugation (ripples) of the sample surface and act as a moving grating for the incident light. The phonon diffracts light inducing a frequency shift by the principles of Bragg’s Law and the Doppler Effect. Light scatters inelastically from these ripples, with energy proportional to the phase velocity of the wave, analogous to the Doppler Effect. Ripple scattering is illustrated in Figure 23, where the Brillouin mode results from Bragg-like scattering from the surface phonons. The condition for Brillouin scattering from surface phonons is constructive interference from the ripple, where the component of the phonon parallel to the backscattering direction is an integral number \( m \) of \( \lambda/2 \).
Elasto-optic coupling is the scattering of light from bulk-like waves through the phonon-induced modulation of the dielectric tensor of the medium. A depolarized spectrum only contains modes from elasto-optic coupling, not the ripple effect.

2.3.2 Relating Sound Velocities to Mechanical Properties

This dissertation concerns scattering events from optically isotropic, transparent organic and inorganic media, for which Brillouin theory is well developed.\(^{129}\) Brillouin scattering of transparent, isotropic samples yields longitudinal \(V_L\) and transverse \(V_T\) sound velocities from inelastic frequency shifts \(\nu\) of light scattered by thermally excited acoustic phonons.

For an isotropic material, only \(V_L\), \(V_T\), and density \(\rho\) are needed to define the total set of elastic constants, the two independent elastic tensors of modulus \(c_{11}\) (longitudinal modulus, \(M\)) and \(c_{44}\) (shear modulus, \(G\)), through the relationships\(^{130}\)
\[ c_{11} = c_{22} = c_{33} = \rho V_L^2 = M \quad (2.21) \]

\[ c_{44} = c_{55} = c_{66} = \rho V_T^2 = G \quad (2.22) \]

In materials with hexagonal symmetry, \( c_{66} \) is a linear combination of \( c_{11} \) and \( c_{12} \) and yields the shear elastic constant associated with \( V_T \) in a perpendicular direction to \( c_{44} \):

\[ c_{66} = 1/2(c_{11} - c_{12}) = \rho V_{T,\perp}^2 \quad (2.23) \]

Bulk modulus \( K \) is a measure of the response of the material’s change in size due to isotropic pressure, and is related to \( M \) and \( G \) by \( K = M - 4/3G \), or from \( V_L \) and \( V_T \) by

\[ K = \rho \left[ \frac{3V_L^2 - 4V_T^2}{3} \right] \quad (2.24) \]

Young’s modulus \( E \), also known as tensile modulus or modulus of elasticity, is defined as the ratio of stress to strain components in a uniaxial direction of mechanical elongation or compression. For an isotropic material, Young’s modulus can be expressed in terms of the bulk and shear moduli as

\[ E = \frac{9KG}{3K + G} \quad (2.25) \]

or in terms of velocities

\[ E = \rho V_T^2 \left[ \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \right]. \quad (2.26) \]

The bulk modulus is typically much greater (3 to 4 times) than the shear modulus. In cases where \( K \to \infty \) in the limit of incompressibility, the approximation for Young’s modulus of \( E = 3G \) is appropriate. Poisson’s ratio \( \sigma \), the ratio of lateral contraction to elongation, approaches \( \sigma = 0.5 \) in this limit and is expressed in terms of moduli by
\[
\sigma = \frac{(3K - 2G)}{(6K + 2G)} ,
\]
and in terms of velocities by
\[
\sigma = \frac{V_L^2 - 2V_T^2}{2(V_L^2 - V_T^2)}.
\]

2.3.3 Acoustic Phonons in Thin Films

It is evident from the elasticity relationships above that interpretation of sound velocities from Brillouin frequency shifts depends on the longitudinal or transverse nature of the phonon. Interpreting the nature of phonon propagation is especially important for extracting sound velocities from Brillouin spectra of phonons confined in nanostructured materials. This section discusses phonon propagation in thin films, in which surfaces and interfaces create localized and guided acoustic waves.

Free-standing thin films with two air interfaces (no substrate) are called unsupported films and are also referred to in the literature as plates. Films adhered to a substrate are called supported films or layers. The surfaces and interfaces of thin films create boundary conditions for sound wave propagation, where velocities of film-guided modes depend on the elastic constants of both the film and the surrounding media, giving rise to a discrete spectrum. Modes in the discrete spectrum of supported films are defined as modes with velocity less than the transverse velocity of the substrate.\textsuperscript{128} Displacements of transverse modes in thin films can have surface guided modes polarized normal to the film (in the sagittal plane, shear vertical, SV) or in the plane of the film (shear horizontal,
SH). SV and SH transverse modes guided in a film or plate can be visualized as in Figure 24.

Figure 24  Partial wave pattern of longitudinal guided (L) and shear vertical (SV) modes (left) and shear horizontal (SH) modes (right) propagating in the film plane.

Acoustic wave propagation theory is well developed for thin films, both unsupported (plate modes) and supported films (layers).\textsuperscript{130,133} Surface acoustic modes are named for their discoverers whose interests were in seismology. Lord Rayleigh is considered to be the pioneer of the field of surface waves, after whom is named the lowest frequency surface wave for supported films and bulk media, the Rayleigh wave.\textsuperscript{134} For unsupported films, Lamb\textsuperscript{135} was the first to observe surface-guided modes polarized in the sagittal plane and Love\textsuperscript{136} was the first to observe shear horizontal modes. In supported films, pure film vibrations become coupled with elastic waves from the substrate, a phenomenon originally studied by Sezawa.\textsuperscript{137} Surface-guided modes in supported films are called generalized Lamb (or Rayleigh, Rayleigh-type, or Sezawa) and generalized Love modes. Stoneley studied interface modes, that are only observable when transverse velocity of the film $V_T$ is approximately equal to the transverse velocity of the substrate $V_T$.\textsuperscript{138}
Film-guided waves exist in films with thickness $d$ on the order of or less than $\lambda_{ph}$. Guided elastic waves are dispersive, meaning that phase velocity depends on the frequency of the phonon. Measured velocities $V$ of dispersive waves depend on the scattered wavevector $Q$, and are most frequently plotted as a function of the dimensionless parameter $Qd$. The full expression for calculating elastic wave propagation in thin films, for waves with sagittal-plane mechanical displacements and where both the film and substrate are isotropic and non-piezoelectric, is represented by the matrix equation 2.29.$^{130}$
\[
\begin{pmatrix}
\& b^{(5)} & -1 & -b^{(5)} & -1 & -b^{(6)} & 1 \\
\& -1 & -b^{(6)} & b^{(6)} & 1 & b^{(6)} & 1 \\
\& 1 - b^{(5)2} & 2b^{(6)} & 1 - b^{(5)2} & -2b^{(6)} & -r(1 - b^{(6)2}) & -2rb^{(6)} \\
\& 2b^{(6)} & -(1 - b^{(5)2}) & -2b^{(5)} & -r(1 - b^{(5)2}) & -2rb^{(5)} & r(1 - b^{(6)2}) \\
\& (1 - b^{(5)2}) \exp(ikb^{(5)}h) & 2b^{(6)} \exp(ikb^{(6)}h) & (1 - b^{(5)2}) \exp(-ikb^{(5)}h) & -2b^{(6)} \exp(-ikb^{(6)}h) & 0 & 0 \\
\& 2b^{(6)} \exp(ikb^{(5)}h) & -(1 - b^{(5)2}) \exp(ikb^{(5)}h) & -2b^{(6)} \exp(-ikb^{(6)}h) & -(1 - b^{(5)2}) \exp(-ikb^{(6)}h) & 0 & 0 \\
\end{pmatrix} \begin{pmatrix} C_5 \\ C_6 \\ C_7 \\ C_8 \\ C_9 \\ C_{10} \end{pmatrix} = 0
\]
where $b^{(5)}$ and $b^{(6)}$ relate to sagittal motion in the film (Figure 24a),

$$b^{(5)} = +i\left[1 - \left(V/V'_T\right)^2\right]^{1/2}$$

(2.30)

$$b^{(6)} = +i\left[1 - \left(V/V'_L\right)^2\right]^{1/2}$$

(2.31)

$b^{(c)}$ and $b^{(d)}$ relate to sagittal motion in the substrate,

$$b^{(c)} = -i\left[1 - \left(V/V_T\right)^2\right]^{1/2}$$

(2.32)

$$b^{(d)} = -i\left[1 - \left(V/V_L\right)^2\right]^{1/2}$$

(2.33)

and $r = c_{44}/c_{44}'$ is the ratio of shear elastic constants for the substrate and film. The surface wave velocities of a supported film are thus strongly dependent on the transverse and longitudinal velocities of the film ($V'_T, V'_L$) and substrate ($V_T, V_L$). The roots of equation 2.29 can be calculated using the Mathematica program in Appendix A.

Surface waves with mechanical displacements perpendicular to the surface, also called polarized in the sagittal-plane, are called Rayleigh or Rayleigh-type waves, the lowest of which is known simply as the Rayleigh wave. The Rayleigh velocity, defined in the asymptotic short wavelength limit (high $Qd$), is directly related to transverse sound velocity and thus mainly reflects shear modulus. Rayleigh velocity $V_R$ on the surface of a material is slightly less than transverse velocity by an amount that depends on the ratio of transverse to longitudinal velocities, as shown in Figure 25. As a first approximation, for a typical polymer with Poisson’s ratio $\sigma = 0.33$, $V_L = 2V_T$ and $V_R \sim 0.93V_T$. 
Figure 25  Velocity normalized to transverse velocity of a Rayleigh wave on the free surface of an isotropic material. (Reprinted from Ref. 130, “Elastic wave propagation in thin layers,” with permission from Elsevier.)

More completely, the equation relating Rayleigh velocity $V_R$ to the transverse $V_T$ and longitudinal $V_L$ velocities of the film is

$$
(2 - \left(\frac{V_R}{V_T}\right)^2)^2 = 4 \left(1 - \left(\frac{V_R}{V_L}\right)^2\right)^{1/2} \left(1 - \left(\frac{V_R}{V_T}\right)^2\right)^{1/2}
$$

(2.34)

and is included in the Mathematica code in Appendix B.

The mechanical displacements of the Rayleigh wave decay exponentially to negligible values within a few wavelengths of the surface. Figure 26 illustrates the increase of penetration depth with phonon wavelength for Rayleigh-type waves in a supported film. Correspondingly, velocities of short wavelength phonons more accurately reflect the elasticity of the film, whereas the velocities of long wavelength phonons are strongly influenced by the elastic properties of the substrate. In the short wavelength limit (high $Qd > 2\pi$), the velocities of the Rayleigh and Sezawa waves asymptotically approach the Rayleigh and transverse velocities of the layer, respectively.
When \( Q_{\parallel}d \approx 2\pi \) or smaller, surface modes with relatively long wavelengths (phonon wavelength comparable to film thickness, \( \lambda_{ph} = \frac{2\pi}{Q_{\parallel}} \approx d \)) are probed and Rayleigh-type velocities start to probe the elastic constants of the underlying substrate.

For supported films, the film can have either a damping (\( i.e. V_T < V_T \), the layer loads the substrate) or a stiffening (\( i.e. V_T > V_T \), the layer stiffens the substrate) effect. In damping supported films, the lowest frequency mode is the Rayleigh mode and the second Rayleigh-type mode is the Sezawa mode. The lowest frequency Rayleigh mode in a damping layer increases as \( Qd \) decreases, but does not exceed the Rayleigh velocity of the substrate. A typical dispersion of a Rayleigh mode on the surface of a damping film is shown in Figure 27.
Rayleigh-type modes are mixtures of transverse and longitudinal modes. The transverse and longitudinal components of Rayleigh-type modes are indicated by the horizontal and vertical axes, respectively, of the ellipses in Figure 28. The Rayleigh mode is mainly transverse while higher frequency Rayleigh-type modes (Sezawa, or S1, S2, etc.) have a more significant longitudinal component (Figure 28).\textsuperscript{139}

The longitudinal and transverse components of waves in the discrete spectrum are localized at the film surfaces.\textsuperscript{140} Frequencies above the substrate transverse sound velocity belong to the continuous spectrum of so-called mixed modes. Mixed modes are often called leaky modes, because they result from energy leaking from the film into the substrate through bulk expansion.\textsuperscript{141}
The dispersion relations for Rayleigh-type modes in unsupported films (plate modes) are obtained by eliminating the first two rows and last two columns of the matrix in equation 2.29, corresponding to removing the substrate material.

Equation 2.35, solved using the Mathematica program in Appendix C, is the dispersion relation for the lowest frequency sagittal-plane mode for an unsupported film, the zero order antisymmetric Lamb wave (flexural wave).\(^{130}\)

\[
\tan \left[ Q \frac{d}{2} \left( 1 - \left( \frac{V_{Lamb}}{V_L} \right)^2 \right)^{1/2} \right] = \frac{4 \left( (1 - \left( \frac{V_{Lamb}}{V_L} \right)^2 ) \left( 1 - \left( \frac{V_{Lamb}}{V_T} \right)^2 \right) \right)^{1/2}}{\left( 1 - \left( \frac{V_{Lamb}}{V_L} \right)^2 \right)^2} \tan \left[ Q \frac{d}{2} \left( 1 - \left( \frac{V_{Lamb}}{V_T} \right)^2 \right)^{1/2} \right] \]

(2.35)

At large values of \( Qd \), Equation 2.35 reduces to the expression for the Rayleigh wave. The lowest velocity Lamb mode differs from higher order modes in that its phase velocity...
decreases to zero at the limit $Qd \to 0$, as noted by the lowest order antisymmetric mode $A_o$ in Figure 29.

Modes with displacements perpendicular to the sagittal displacements of Rayleigh, Sezawa, and Lamb modes are called shear horizontal (SH) modes (Figure 24b).

![Phase velocity dispersion curves for an unsupported film (quartz). Notice particularly the unique dispersion of the lowest velocity Lamb mode, $A_o$. (Reprinted from Ref. 130, “Elastic wave propagation in thin layers,” with permission from Elsevier.)](image)

**Figure 29** Phase velocity dispersion curves for an unsupported film (quartz). Notice particularly the unique dispersion of the lowest velocity Lamb mode, $A_o$. (Reprinted from Ref. 130, “Elastic wave propagation in thin layers,” with permission from Elsevier.)

SH waves belonging to the discrete spectrum ($V < V_T$) are known as Love waves. The following equation, evaluated using the Mathematica program in Appendix D, describes the dispersion relationship for real values of Love mode velocities $V_{Love}$ in damping films when $V_T < V < V_{T}^{'}$:

$$\tan[Qd \left(\frac{V_{Love}}{V_T} - 1\right)^{1/2}] = r \frac{(1 - \left(\frac{V_{Love}}{V_T}\right)^2)^{1/2}}{\left(\frac{V_{Love}}{V_T}\right)^2 - 1}^{1/2}$$

(2.36)
2.3.4 Brillouin Scattering for Thin Films

The theory for Brillouin scattering has been developed for unsupported\textsuperscript{142,143} and supported\textsuperscript{144,145} thin films. Brillouin spectra can be used to infer the nature of the surface and film-guided phonons and the elastic properties of the film material through analysis of polarization and scattering wave vector dependence. In transparent thin films as considered here, scattering occurs via the ripple mechanism at both film interfaces and elasto-optic coupling within the film.

Analysis of incident and scattered light polarization can help identify the nature of modes observed in Brillouin scattering. In \textit{p-p} polarization, waves with displacements in the sagittal plane (SV) are selected, which include Rayleigh, Sezawa, and higher frequency generalized Lamb waves. In \textit{p-s} polarization, shear horizontal (SH) displacements are selected and Love modes of thin films are observed.\textsuperscript{146} Scattering from Love modes occurs only by elasto-optic coupling. In Figure 30, Brillouin spectra are compared for scattering without an analyzer (\textit{p-ps}) and with \textit{p-p} and \textit{p-s} polarization for a silicon oxynitride layer on gallium arsenide.\textsuperscript{146} The Brillouin mode near 10 GHz is the Rayleigh mode (shear vertical) and the mode near 13 GHz is a Love mode (shear horizontal).
Figure 30  The lower three lines are Brillouin spectra from a 2 µm film (silicon oxynitride on gallium arsenide) collected under three polarization conditions. The top two lines are calculated resonances for longitudinal and shear horizontal components.  (Reprinted figure with permission from Ref. 146.  Copyright 2000 by the American Physical Society.)

In summary, thin films have film guided waves that are dispersive and have longitudinal and transverse components.  Sagittal-plane modes are referred to as Lamb modes if the surfaces are free surfaces, i.e. boundaries are not restricted, and Rayleigh-type or Sezawa waves in supported films. Dispersion curves (phonon frequency or velocity vs. $Q_{id}$) for isotropic materials are uniquely defined by 2 quantities: transverse and longitudinal velocities. These two velocities uniquely define all the elastic constants through the relationship $V_i = \sqrt{c_i / \rho} = \frac{V_o \lambda_o}{2 \sin(\theta)}$ where $V$ is phonon velocity, $c$ is elastic modulus, $i = L,T$, $\rho$ is mass density, $V$ is Brillouin frequency, $\lambda_o$ is incident wavelength, and $\theta$ is the angle between the incident light and the surface normal. Specific interpretations of acoustic waves from Brillouin scattering in thin films are presented in the following sections.
2.3.4.1 Unsupported Films

Using Brillouin light scattering, Forrest et al. measured the mechanical properties of unsupported (free-standing) PS films with thicknesses ranging from less than to greater than the average unperturbed end-to-end dimension of the molecules, $R_{EE}$. The Brillouin spectra contained many peaks corresponding to antisymmetric (A) and symmetric (S) Lamb waves of unsupported films, as labeled in the spectrum in Figure 31.

Varying the scattering angle $Q_{\|} = 4\pi \lambda (\sin \theta)$ allows analysis of the dispersion relationship of the Lamb waves, that is their frequency or velocity dependence on scattering wave vector.

Figure 31 Brillouin spectrum for an unsupported PS film with thickness $d = 190$ nm and $Q_{\|} = 12.2$. Antisymmetric (A) and symmetric (S) Lamb modes are labeled. (Reprinted figure with permission from Ref. 76. Copyright 1998 by the American Physical Society).
Dispersion relations for thin films are typically expressed as a function of the dimensionless parameter $Q||d$, where $d$ is the film thickness. Elastic constants for unsupported PS films were obtained by fitting phonon velocity dispersion curves, as in Figure 32, using matrix equation 2.29.

![Figure 32](image)

**Figure 32** Velocity dispersion data for unsupported PS films with thicknesses equal to and less than $d = 190$ nm, with corresponding calculated curves using best fit elastic constants $c_{11} = 5.65$ GPa and $c_{44} = 1.40$ GPa. (Reprinted figure with permission from Ref. 76. Copyright 1998 by the American Physical Society).

Using the longitudinal velocity the authors measured for bulk polystyrene $V_L = 2.44$ km/s and assuming bulk density $\rho = 1.056$ g/cm$^3$, they varied $V_T$ to obtain a fit to the data. For thick films ($d > 170$ nm), they obtained elastic constants in agreement with bulk PS, $c_{11} = \rho V_L^2 = 5.65 \pm 0.09$ GPa and $c_{44} = \rho V_T^2 = 1.40 \pm 0.03$ GPa. Surprisingly, when they extended this technique to films that exhibited a decrease from bulk $T_g$ of 65 K ($M_w = 767$ kg/mol), they did not observe a deviation from bulk elastic constants. In particular, the authors monitor the frequency of the $S_o$ mode. For unsupported films, $S_o$ is the ideal acoustic phonon to use for detailed comparison of very thin unsupported films because its velocity does not diverge as $Qd$ approaches zero. In addition to mechanical stiffness, they also conclude that room temperature mass density and thermal expansion
of the glassy state PS films are consistent with bulk values independent of film thickness as low as 29 nm.

2.3.4.2 Supported Films

Interpretation of Brillouin spectra from supported thin films depends on the ratios of shear velocities between the substrate and the film. For cases studied in this work (polymer thin films on a silicon oxide substrate, viruses on Si or Al, and silicon oxide on Si), acoustic modes exist under the conditions for a damping film, for which the transverse velocity of the film $V_T^f$ is less than that of the substrate $V_T$. The case for which the inverse is true, referred to as stiffening films, will not be considered here.

Sun et al. used Brillouin light scattering to determine the elastic constants of polystyrene thin films on a silicon wafer. The Brillouin spectra look similar to those from unsupported films in Figure 31, but modes in supported films do not have well defined symmetry. Instead of Lamb waves, supported films have a Rayleigh mode and higher order Sezawa modes, labeled in Figure 33 as detected using three free spectral ranges.
Figure 33 Brillouin spectra of a 173 nm PS film on Si at $\theta = 70^\circ$ and free spectral ranges a) 10 GHz, b) 15 GHz, and c) 30 GHz. The peaks are labeled as Rayleigh (R), first Sezawa (S1), second Sezawa (S2), and third Sezawa (S3). The small peak in a) between S1 and R is an instrumental ghost. (Reprinted figure with permission from Ref. 69. Copyright 1994 American Institute of Physics.)

As with unsupported films discussed above, measurements were performed on films with several ($d = 173$ nm, 245 nm, and 375 nm) thicknesses at various incident angles ($\theta = 30^\circ, 40^\circ, 50^\circ, 60^\circ, 70^\circ$) to explore a wide range of $Q_\parallel d$. The results from the two thinnest layers were combined with data from 58 nm and 114 nm films in Reference 75 and the dispersion curves and experimental velocities are plotted in Figure 34. It is immediately evident that a single set of elastic constants can be used to fit the velocities in PS films supported on Si with thickness as low as 58 nm.
Figure 34  Velocity dispersion curves for PS film supported on Si with symbols representing \( d = 58 \) nm (X), 114 nm (triangles), 173nm (filled circles), and 245 nm (empty circles). (Reprinted figure with permission from Ref. 75, “Brillouin Light Scattering Studies of the Mechanical Properties of Polystyrene/Polyisoprene Multilayered Thin Films.” Copyright Wiley-VCH Verlag GmbH & Co. KGaA.)

Assuming a bulk density of \( \rho = 1.056 \) g/cm\(^3\), Sun et al. found the best fit elastic constants to the experimental data to be \( c_{11} = 5.7 \pm 0.15 \) GPa and \( c_{44} = 1.39 \pm 0.03 \) GPa.\(^{69}\)

Sun et al. used estimates of the root-mean-square end-to-end distance \( R_{EE} = \langle R^2 \rangle^{1/2} = N^{1/2}L \) of PS in solution (where \( R \) is the distance between chain ends in a particular conformation of a chain consisting of \( N \) segments each of length \( L \)) to compare their film thicknesses to the average size of polymer molecules. From the measured value of \( \langle R^2 \rangle / \overline{M}_n \rangle^{1/2} = 7.35 \) nm for monodisperse PS\(^{147,148}\) and neutron diffraction data that shows PS molecules are approximately the same size in the solid state as in solution,\(^{148}\) they estimate \( R_{EE} = 13 \) nm for their molecular weight of \( M_w = 30 \) kg/mol and \( R_{EE} = 57 \) nm for \( M_w = 600 \) kg/mol. Therefore, even in the thinnest film of 58 nm, \( (M_w = \)
767 kg/mol, $R_{EE} \sim 61$ nm), they concluded the film thicknesses were sufficiently large to prevent thickness dependent film properties.

Forrest et al. continued the progress of Sun et al. and investigated the mechanical properties of PS and polyisoprene (PI) multilayers in which the individual layer thicknesses were as low as 16 nm. Utilizing a multilayered system, the total film thickness was made large enough (~160 nm) to investigate the $Q|d$ range from 2 to 4, where the differences in film-guided velocities were large and distinguishable (Figure 34). In contrast, measurements of single layers with similar thickness would probe the $Q|d$ range from 0.2 to 0.4, where the Rayleigh and higher order mode velocities are very similar (Figure 34), seriously compromising the sensitivity of Brillouin scattering to detect small changes in elastic constants. In systems with individual layer thicknesses less than one third the unperturbed $R_{EE}$ of the molecules, in which molecular shapes are necessarily oblate, they observed very small (<20%) changes in the elastic constants.

For the above studies and those of other transparent supported films, the penetration of light can complicate the interpretation of Brillouin spectra, because scattering occurs from at least three mechanisms. Ripple scattering can occur at both film interfaces and elasto-optic coupling occurs in the film. The interference between ripple and elasto-optic contributions makes it difficult to separate and interpret the scattering amplitudes from acoustic waves. Bortolani et al. note that a silica film on silicon is an ideal system to observe strong interference effects between ripple and elasto-optic contributions. They measured the phonon spectrum of a 225 nm film of silica grown on the (001) face of Si using Brillouin light scattering. They observed strong interference between the surface
ripple and the elasto-optic coupling contributions to the BLS amplitude. Ripple scattering occurs at the two interfaces, air-SiOx and SiOx-Si, and elasto-optic coupling occurs in the two materials.

Bortolani et al. performed measurements in backscattering geometry using $p$-polarized light with a wavelength of 514.5 nm and incident power $\sim$250 mW. The collection aperture was f/1.8. They used a free spectral range of 60 GHz to simultaneously capture frequencies below the transverse acoustic bulk phonon of SiO$_2$ ($\nu = 13.3$ GHz, $V_{T,\text{SiO}_2} \sim 3.7$ km/s) and above the longitudinal threshold of Si (30.2 GHz). In the spectrum in Figure 35, they identify the Rayleigh mode with velocity just below $V_T$ for bulk SiO$_2$ (RW), what they call a Sezawa-Lamb wave structure extending below the bulk $V_T$ for Si ($V_{T,\text{Si}} \sim$5.65 km/s) (SW-LW1), and the broad structure from 25-40 GHz belonging to the continuous spectrum of the substrate.\textsuperscript{149}

![Figure 35](image_url)  

Figure 35  Brillouin spectra from a 225 nm silica film on Si measured at $\theta = 67^\circ$ (Reprinted figure with permission from Ref. 149. Copyright 1982 by the American Physical Society).
Based on polarization dependences of the real and imaginary contributions to the ripple and elasto-optic contributions, Bortolani et al. deciphered the relative intensities from interfering surface and interface ripples with each other and with elasto-optic modes in the film. This work implies that interpretation of spectrum from silica films or structures on silicon for the purpose of extracting mechanical moduli will require substantial interpretation.

2.3.4.3 Shear Horizontal Waves

In addition to the Rayleigh and Sezawa modes polarized in the sagittal plane (shear vertical, SV), Brillouin measurements of some supported film structures and buried layers contain shear horizontal (SH) modes. SH modes have been observed less frequently, with concentration of evidence for buried layer (silicon-on-insulator, SOI) and oxide or nitride on semiconductor structures. Brillouin scattering from SH waves occurs purely by elasto-optic scattering. SH modes provide elastic constant information that is inaccessible via SV modes, and they can be identified as the Brillouin peaks from thin films appearing in p-s polarization.

Bell et al. were the first to observe shear horizontal modes using Brillouin scattering. Bottani et al. were the first to observe SH phonons in the continuum spectral region, while also observing discrete SH modes (Love waves) for a buried SiO$_2$ layer. Interpreting the spectrum and calculating the layer projected phonon density of states from SH waves, they determined the discrete SH mode is confined to the layer while the continuum region of the spectrum shows a main quasi-resonance (or pseudo-
Carlotti et al. used shear horizontal modes traveling parallel to the surface of ~1 µm polycrystalline AlN and ZnO films to calculate the elastic constant $c_{66}$ which is inaccessible from SV waves. Panella et al. used SH modes to help identify five independent elastic constants in InSe films.

In silicon oxynitride films (thicknesses of 1, 2, and 3 µm) on gallium arsenide substrates, a mode was observed in $p$-$s$ polarization that was identified as a shear horizontal resonance in the thin film. Interestingly, in this same structure, a Brillouin peak was observed with frequency lower than that of the Rayleigh surface wave. In fact, a soft interfacial layer between the film and substrate was observed by electron microscopy. The authors postulated the mode was confined to a soft interfacial layer with thickness ~40nm. They determined that a low frequency Brillouin mode could be observed if an interfacial layer existed with thickness ~40nm if the interfacial shear modulus is ~37% that of the oxynitride film.

Calculations have revealed surface acoustic waves with “predominantly” SH polarization propagating along grooves of a shallow periodic grating. The authors use the term “predominantly” because surface waves propagating along shallow grooves cannot exist with either pure shear vertical or shear horizontal polarization. Instead, the stress-free boundary conditions create modes with mixed SV and SH polarizations.

Most studies of periodic grooves concentrate on the surface-grating-induced zone folding of phonons propagating perpendicular to the grooves, where measurements are denoted with a wave vector $q_{\perp}$. Dutcher et al. found that the Rayleigh wave velocities measured for $q_{\perp}$ were ~4% lower than those measured for $q_{\parallel}$, where $q_{\parallel}$ denoted phonon wave vector parallel to the grooves. Further, the Rayleigh velocities for $q_{\parallel}$...
indicated no change in bulk Si shear modulus, possibly indicating that the modulus in the
direction perpendicular to the grooves decreases very slightly from the bulk. Dutcher et al. did not observe any peaks in p-s polarization (depolarized scattering) for either \( \mathbf{q} \), despite predictions from reference 112.

Most studies of Brillouin spectra to estimate elastic constants have been
performed on unsupported, supported, and buried thin films. For isotropic materials, the
Rayleigh velocity and longitudinal resonances are enough to calculate the two
independent elastic constants, \( c_{11} \) and \( c_{44} \). Additional elastic constants measured for
polycrystalline materials used shear horizontal modes to calculate additional elastic
constants such as \( c_{66} \). A few studies used Brillouin spectroscopy for more complex
structures, shallow grooves of a Si wafer, and a new phenomenon of hybridization of the
Rayleigh mode and the longitudinal resonance resulted in zone-folding and a phononic
band-gap. The principles from the above described studies will provide insight into
Brillouin spectra collected in this work for polymeric and silicon oxide structures subject
to two dimensions of nanoscale confinement.

2.3.5 Non-propagating Resonances

Spectroscopic techniques can probe resonant vibrational modes of individual
particles with length scales comparable to the phonon wavelength.\textsuperscript{157} Photon-phonon
coupling leads to inelastic frequency shifts associated with acoustic wave propagation or
nanoparticle resonant frequencies. Raman spectroscopy, which detects frequencies from
about 100 to \( 10^5 \) GHz, is a useful tool for size characterization of carbon nanotube
Brillouin spectroscopy has been used as an effective tool to measure acoustic phonons of nanostructures including inorganic\textsuperscript{161} and polymeric\textsuperscript{162} nanospheres and carbon nanotubes.\textsuperscript{163} As discussed in section 2.2.2, some have calculated the vibrational eigenfrequencies of geometrically cylindrical and spherical virus particles.\textsuperscript{107} The size, shape, and composition of virus particles cause them to resonate in the gigahertz frequency range, which is detectable by Raman\textsuperscript{164} and possibly Brillouin spectroscopy.

Single walled carbon nanotubes (SWNTs) are excellent examples of nanostructures with distinct vibrations, well studied by Raman spectroscopy.\textsuperscript{165} For example, the radial breathing mode frequency $\omega_{RBM}$ is inversely dependent on the diameter $d_{SWNT}$ of the SWNT, $\omega_{RBM} = 223.75$ (cm$^{-1}$ nm)/$d_{SWNT}$ (nm), typically in the range 100-300 cm$^{-1}$.\textsuperscript{158} Brillouin spectroscopy can also be used to measure acoustic phonon propagation. Bottani et al. estimated Young’s modulus $E \sim 1$ TPa from a broad Brillouin mode centered at $\sim$45 GHz for oriented SWNTs.\textsuperscript{163} They further infer from the disappearance of this mode when the SWNTs are rotated 90°, perpendicular to the scattering wave vector, that the tubes are essentially independent and cannot be considered a homogeneous medium, at least at the scale of the laser wavelength (514.5 nm).

Vibrational spectroscopy can also detect elastic waves of spheres. Theory of acoustic modes confined in a homogeneous elastic sphere with a free surface was first formulated by Lamb, who predicted two types of modes, namely, the spheroidal (spherical if $l = 0$; and ellipsoidal with longitudinal and transverse displacements if $l = 2$)\textsuperscript{166} and torsional modes.\textsuperscript{167} Lamb’s theory is applicable if coupling of the spheres with
the surrounding matrix medium does not exist, a so-called free-sphere model. The modes of a sphere are labeled by the angular momentum number \( l \) and the index or harmonics number \( n \). The modes of an elastic sphere with diameter \( D \) is given by the following expression,\(^\text{169}\)

\[
V_{l,n} \approx S_{l,n} \frac{V}{D}
\]

(2.37)

where \( V \) is the sound velocity of the sphere denoted \( L \) for longitudinal and \( T \) for transverse. \( S_{l,n} \) is a scaling parameter with a value \( \sim 1 \) depending on the vibrational mode. It is worth noting that based on the theoretical group selection rules for light scattering,\(^\text{168}\) only the spheroidal (spherical and ellipsoidal) modes with \( l = 0 \) or 2 can be observed, while observation of torsional modes should be precluded in the light scattering spectrum. However, these selection rules can be relaxed for anisotropic materials or under resonant excitation.

Recent experiments revealed that in a three dimensional ordered array of monodisperse SiO\(_2\) spheres, measurements made in \( p-p \) and \( p-s \) polarization configurations yielded identical Brillouin spectra.\(^\text{161}\) The vibration of the lowest frequency spheroidal and torsional modes \( (l = 2) \) are practically equal, and correspond to the completely depolarized mode, that is, the quadrupolar fundamental mode \( (l = 2, n = 0) \), where \( S_{2,0} \sim 0.85 \).\(^\text{169}\) The displacement fields of these low energy spheroidal modes are pictured in Figure 36. Low energy torsional vibrations, degenerate with the low energy spheroidal modes in solid spheres, induce shear strength.\(^\text{168}\) The lowest energy odd (left) and even (right) torsional modes can be visualized as in Figure 37.
Inelastic light scattering allows direct, non-contact, non-destructive measurement of the mechanical properties of the individual unit and its assembly. Brillouin light scattering has been successfully applied to polymer colloid particles.\textsuperscript{110,111} The group of Fytas has studied the vibrational spectrum of polymeric and silica spheres,\textsuperscript{111} giant starlike micelles,\textsuperscript{171} and the effects of surrounding environment on their vibrational properties.\textsuperscript{172} They found hypersonic phononic bandgaps in colloidal crystals of polystyrene spheres, with tunable frequency via fluid infiltration.\textsuperscript{172} Interestingly, for starlike micelles in solution, Brillouin spectra contained a $Q$-dependent low frequency
phonon with longitudinal velocity similar to the solvent and a $Q$-independent mode associated with the $l = 2$ spheroidal harmonic of the PS core.\textsuperscript{171} The frequency dispersion of the modes is shown in Figure 38, and the inset shows the form factor for these PS-PI block copolymer micelles in n-decane with a PS core radius ~58 nm and overall radius ~353 nm.

![Figure 38](image.png)

Figure 38  Frequency dispersion of soft starlike particles with effective volume fraction $f$~0.1 in n-decane, showing the $Q$-independence of the high frequency mode ~6.3 GHz and the $Q$-dependent low frequency mode associated with the longitudinal velocity of the solvent. The inset shows the form factor with an illustration of the starlike micelle. (Reprinted figure with permission from Ref. 171. Copyright 2000 by the American Physical Society.)

The presence of a $Q$-independent mode indicates a localized vibration while the $Q$-dependent mode indicates acoustic phonon propagation. In the above case, the authors concluded that the $Q$-independent vibration was localized within the PS core. The group of Kuok has measured $Q$-independent acoustic modes confined in silica particles. Fitting their Brillouin spectra with the eigenvalue equation from Tamura \textit{et al.},\textsuperscript{173} they estimated sound velocities and actually found a decrease in Young’s modulus ~60% from bulk silica for particles from 140 \(\mu\)m down to ~4 \(\mu\)m.\textsuperscript{174} They account for this decrease by including
in their calculations a pore volume fraction $f \approx 11\%$, not a confinement induced change in the particle modulus.

Recent interest in using viruses as self-assembly units in nanotemplates for electronic and photonic applications has spawned calculations and measurements of vibrational eigenmodes in viruses. Talati and Jha, assuming elasticity of viruses similar to the crystalline protein lysozyme ($E \approx 2.7$ GPa), calculated vibrational frequencies of spherical viruses. These calculations estimate behavior similar to an elastic sphere with a low frequency mode at $\sim 3$ GHz for a 150 nm virus.$^{107}$

Fonoberov and Balandin calculated vibrational modes of the RNA containing, cylindrical tobacco mosaic virus (TMV) using the same lysozyme parameters.$^{175}$ The breathing mode eigenfrequencies are inversely proportional to the diameter of the tube, which is 18 nm for TMV. For filled and empty cylindrical virus rods, in air and in water, the lowest radial breathing mode frequency for TMV was in the range of 1.8-2.3 cm$^{-1}$ ($\sim 55-70$ GHz).

Recently, an acoustic vibration of the cylindrical M13 bacteriophage virus was observed using Raman spectroscopy.$^{164}$ Using the atomistic structure of the capsid, the authors estimated M13 to have an inner channel of 3.8 nm and outer diameter 6.8 nm.

![Figure 39](image-url)

Figure 39  Visualization of the displacement pattern for the Raman-active axial torsion mode of the M13 phage protein coat (After Ref. 164).
Comparing their results to elastic continuum theory, the authors ascribed the mode at \( \sim 8.5 \text{ cm}^{-1} \) (~250 GHz) to an axial torsion mode of the M13 phage protein coating, as pictured in Figure 39. They suggest Raman spectroscopy may be a useful tool to monitor functionalization of the coating and/or self-assembly of the phages. Vibrational spectroscopy is commonly used to determine length scales of particles with known elasticity. Raman and Brillouin scattering may also provide elasticity information about biological nanostructures with well known sizes, such as virus particles as discussed above. The Brillouin frequencies and elastic moduli estimates of a DNA containing spherical virus are discussed in Chapter VI.

This chapter has discussed the necessities and challenges for understanding materials behavior at the nanoscale. Ultimately, better characterization techniques will lead to more advanced fabrication and manipulation of nanoscale features. Mechanical properties are crucial for construction and/or fabrication on any length scale, however the limited number of reliable techniques for characterization of nanoscale materials creates a need for better methods to help advance understanding of size-dependent properties. Light scattering is a particularly useful technique, as a non-destructive means to analyze vibrational states and thus mechanical properties of nanostructured materials. In particular, Brillouin light scattering has quantified elastic constants of a variety of thin films. The focus of the following chapters is to utilize Brillouin light scattering to quantify elastic constants of structures with higher dimensions of confinement, namely lithographically prepared rectangular beams (grating lines), spherical polymeric, and spherical-like biological (virus) particles.
3.1 Tandem Fabry-Perot Interferometer (TFPI)

Brillouin spectra were measured using a Tandem Fabry-Perot interferometer (TFPI) manufactured by JRS Scientific Instruments.\textsuperscript{176} A single Fabry-Perot (FP) interferometer consists of a pair of highly reflective parallel mirrors designed to induce multiple reflections of light between the mirror surfaces. The FP only transmits light that interferes constructively at the mirror surfaces, satisfying the equation

\[ L = \frac{p\lambda}{2} \]  

(3.1)

where \( p \) is an integer, \( \lambda \) the wavelength of light, and \( L \) the mirror distance. The difference between consecutive transmitted wavelengths \( \Delta\lambda \), known as the free spectral range (FSR) is shown in Figure 40.
Figure 40  The optical transmission function $T$ and wavelength difference $\Delta \lambda$ of transmitted light through the interferometer (After Ref. 176).

Figure 40 also identifies the full width at half maximum (FWHM) of the transmitted lines $\delta \lambda$. Finesse $F$ is a quality factor related to the mirror reflectivity and flatness, defined experimentally by the expression

$$F = \frac{\Delta \lambda}{\delta \lambda}$$  \hfill (3.2)

The mirror spacing, incoming wavelength, and the finesse determine the transmitted light intensity.\textsuperscript{176}

The FP functions as a spectrometer when the mirror spacing $L$ is scanned such that selected wavelengths satisfying equation 3.1 are transmitted. The spectral range of the FP is thus determined by $\Delta \lambda$, which can be increased by decreasing $L$, as

$$\Delta \lambda = \frac{\lambda^2}{2L}$$  \hfill (3.3)

Practically, however, the finesse, is typically less than 100 due to the quality of mirror substrates and coatings.\textsuperscript{176} Thus, FSR can only be increased a limited amount without sacrificing resolution because $\delta \lambda$ increases with $\Delta \lambda$. Most problematic, however, is the
fact that the measured intensity is a sum of all wavelengths satisfying equation 3.1, that is transmission over multiple orders of mirror spacing. Therefore, unless the spectrum is known \textit{a priori}, interpretation of the Brillouin data remains ambiguous.

The Tandem Fabry-Perot interferometer suppresses higher order transmissions, therefore increasing the effective FSR by introducing a second interferometer (FP2). For the six-pass TFPI used in these experiments, J. R. Sandercock found the optimum ratio between spacings of the second FP (FP2) $L_2$ and the second FP (FP1) $L_1$ to be $\sim 0.95$.\textsuperscript{176} Light transmitted through both FPs must simultaneously satisfy the resonance, or constructive interference, conditions of both FPs, expressed as

$$\lambda = \frac{2L_1}{p} = \frac{2L_2}{q}$$

(3.4)

where $q$ is an integer number for the second FP. A good practical value of $L_2/L_1 = 0.95$ leads to the relationship between integer orders of transmission lines for the two FPs

$$\frac{q}{p} = 0.95$$

(3.5)

This means that 19 neighboring transmission peaks of FP1 are not transmitted by FP2. The $20^{th}$ order of FP1 will also resonate in the cavity of FP2 (the $19^{th}$ order of FP2), allowing transmission through the TFPI. The transmissions of each FP and the TFPI are shown in Figure 41.
Figure 41  The individual transmission intensities of both Fabry-Perot interferometers and that allowed by the tandem Fabry-Perot interferometer (After Ref. 176).

The TFPI designed by Sandercock achieves the above mirror spacing conditions using a single translation stage as shown in Figure 42.

Figure 42  Sandercock design of the single translation stage for a tandem Fabry-Perot interferometer (After Ref. 176).

By introducing the angle $\theta_{FP}$ (shown simply as $\theta$) between the axes of FP1 and FP2, the relationship between $L_1$ and $L_2$ remains constant, $L_2 = L_1 \cos \theta$, during scanning. When
collecting a full spectrum, the stage is scanned across a central line by $L_1 \approx \pm \Delta \lambda$ (between $\lambda_{p-1}$ and $\lambda_{p+1}$, where $p$ is the central transmission order). Further design details of this TFPI create six passes of the light through the tandem interferometers (three times each), where each pass increases signal contrast.

3.2 Experimental Setup

Brillouin scattering spectra of surface waves were measured in back-scattering geometry using a tandem six-pass Fabry-Perot interferometer and an Ar-ion laser with wavelength $\lambda = 514.5$ nm. The monochromatic source was either a Lexel 3500 with Frequency Lock mode or other comparable laser with a single mode operator. An avalanche photodiode (APD) detected the light transmitted by the interferometer. A multi-channel analyzer card binned the signal from the APD into 1024 channels. During measurements, each channel was clocked for 0.5 ms, therefore 2000 sweeps of the multi-channel analyzer equated to 1 sec of photon collection per channel. Most Brillouin data was treated by subtracting dark noise (24 counts/sec or 12 counts/1000 sweeps) and normalizing to counts per second of photon collection per channel. Low sample volume and transparency required in some cases as many as 100,000 sweeps, or 50 seconds of accumulation per channel. One thousand sweeps required ~10 minutes of real measurement time.

Other key elements of the Brillouin setup are identified in Figure 43, including a half waveplate, a polarizer, a backscattering mirror placed at 45°, a focusing aperture just before the sample, and a polarization analyzer just before the final focusing lens of the
optical system that projects the image of the sample into the entrance of the spectrometer/interferometer. Incident polarization was selected as vertical (s-polarization) or horizontal (p-polarization) using the half waveplate and the polarizer. Cases in which no analyzer was used for horizontal incident polarization were denoted $p-ps$ polarization.

The backscattering mirror was either a small fully reflecting mirror or a semi-transparent mirror. The focusing aperture was either a lens (achromatic, f/2) or objective (10x Mitutoyo long-working distance objective, NA=0.28). The working distances of the lens and objective were 76.2 mm and 33.5 mm, respectively. The choice of focusing aperture affected the choice of backscattering mirror.

Figure 43: Schematic of the Brillouin experiment for thin films, gratings, and viruses. Elements consist of 1) 514.5 nm Laser 1b) Frequency Lock Box 2) ~95:5 semi-transparent mirror 3) spatial filter 4) half waveplate 5) polarizer 6) backscattering mirror 7) focusing aperture 8) sample 9) analyzer 10) final focusing lens 11) pinhole 12) tandem interferometer 13) set of mirrors for reference beam (green dashed line).
The small, fully reflective mirror was used in combination with the f/2 lens for measurements of polymer thin films and gratings. It is known that small mirrors in the backscattered beam block a small portion of scattered light\textsuperscript{118} as shown in Figure 44, where the dashed circles represent the parallel beam of collected light. The small mirror blocks a middle range of $Q_{||}$ values, and can create a split of Brillouin modes. The effect of the small mirror was minimal in the case of surface waves in PS and photoresist polymers, because the parallel beam from the f/2 lens was ~30 mm in diameter (Figure 44b). However, the small mirror blocked a more significant portion of the parallel beam from the Mitutoyo 10x objective (diameter ~ 13 mm, Figure 44a) and affected the absolute frequencies of the Brillouin spectra.

Figure 44: A cross-section of the scattered light paths showing the portion blocked by the small backscattering mirror for the (a) Mitutoyo 10x objective and (b) the f/2 lens. The dashed line circles represent the diameters of the parallel beam of backscattered light from the (a) Mitutoyo 10x objective and (b) the f/2 lens.
Some measurements were performed with the 10x Mitutoyo objective and small mirror because the objective resulted in higher signal intensity than the f/2 lens normalized to incident laser power, as shown in Figure 45.

![Figure 45](image_url)

Figure 45 Brillouin spectra of a photoresist polymer film comparing the intensities from experimental setups using the f/2 lens (thick) and the 10x Mitutoyo objective (thin) as the focusing apertures. The intensity is normalized to counts/second/mW.

In some cases, spectra collected using the 10x objective and small mirror were different from when using the 10x objective and semi-transparent mirror. For example, Figure 46 contrasts two cases for a silicon oxide film on silicon using s-polarization, $Q_{||} = 10.3 \, \mu m^{-1} \ (\theta = 25^\circ)$. The frequencies in the spectra collected using the semi-transparent mirror more accurately followed the behavior predicted by theory (discussed in Chapter V), while use of the small mirror resulted in higher frequencies than expected for the surface modes. The character of the longitudinal modes is also different, but the origin of the differences is unclear. The most likely explanation for the surface mode differences is an uneven splitting of the measured $Q$ range by the small mirror.
Figure 46 Spectra from a silicon oxide film on silicon from an experimental setup with the semi-transparent mirror (thick) and the small mirror (thin) as the backscattering mirror.

Although the spectra from the setup with the small mirror resulted in unreliable absolute frequencies from silicon oxide films on silicon, surface mode identification was still possible based on sample and polarization orientations. For example, the small mirror resulted in higher incident beam power, which allowed very clear qualitative analysis for depolarized (p-s polarization) measurements. Figure 47 shows the clear comparison of p-ps to p-s polarization conditions for a silicon oxide film on silicon using the small mirror and 10x objective.
Figure 47  Brillouin spectra of a silicon oxide film on silicon using the small mirror for \(p-p_s\) and \(p-s\) polarization. One mode in the depolarized spectrum \((p-s)\) appears very clearly.

In later measurements of silicon oxide films and gratings, as well as viruses and polymer spheres, a semi-transparent mirror replaced the small mirror as the backscattering mirror to avoid spectral distortions introduced by partial beam blocking. Although it eliminated beam blocking, the semi-transparent mirror caused separate problems. The reflectance of the semi-transparent mirror at 45º incidence was \(\sim 40\%\) for vertically polarized light as compared to \(\sim 20\%\) for horizontally polarized light. The polarization dependent reflection and transmission of the semi-transparent mirror affected measurements in two ways.

First, the low reflection of horizontal light reduced the maximum incident power for \(p\)-polarization measurements. Although previous spectra of silicon oxide films on Si were measured with incident power as high as 250 mW,\(^{149}\) deteriorating conditions of the laser limited these measurements to \(\sim 30\) mW. For this reason, some spectra for films and
gratings and all spectra for viruses, were performed with $s$-polarization, a condition allowing incident power $\approx 90$ mW on the sample. Second, the semi-transparent mirror acts as a partial analyzer. By reflecting two times more $s$-polarized than $p$-polarized scattered light, it artificially increased the intensity ratios of $p$-polarized to $s$-polarized modes.

If stable, high incident laser power is available, performing measurements of inorganic films with the small mirror can eliminate strong losses of $p$-polarization reflection from the semi-transparent mirror. In previous studies of inorganic films, in which incident powers exceeded 150 mW, a vertical slit was used to limit the $Q_{||}$ range of the collection optics. In those cases, the spectral evidence of a broadened, split mode was eliminated, and measurement times ranged from 2-4 hours. In future measurements, a compromise of reliable spectra and reasonable signal intensity may ultimately result from the combination of $f/2$ lens, the small mirror, and a vertical slit. Alternatively, to increase the incident power when using a semi-transparent mirror, a smaller incident angle on the semi-transparent mirror increases the reflection coefficient of horizontally polarized ($p$-polarized) light. A third option would be to use the semi-transparent mirror but rotate the sample vertically (about a horizontal axis), such that vertical polarization corresponds to $p$-polarization.

The magnitude of the wave-vector parallel to the film surface, $Q_{||} = (4\pi\text{Sin}\theta)/\lambda$, was changed by changing the angle $\theta$ between the film surface normal and the incident light. The geometry of the $f/2$ lens allowed a minimum angle of 8° ($Q_{||} = 3.4$ $\mu$m$^{-1}$). For measurements using the 10x Mitutoyo objective, the minimum angle was 15° ($Q_{||} = 6.3$ $\mu$m$^{-1}$). The maximum angle for both focusing apertures varied from $\theta = 67^\circ$ ($Q_{||} = 22.6$ $\mu$m$^{-1}$).
μm⁻¹) to 70° (Q∥ = 24 μm⁻¹). Typically, samples were measured at θ values including the maximum, minimum, and interval angles of 25° (Q∥ = 10.3 μm⁻¹), 35° (Q∥ = 14 μm⁻¹), 45° (Q∥ = 17.3 μm⁻¹), and 55° (Q∥ = 20 μm⁻¹). The Brillouin peak positions were estimated by fitting the spectra with multiple Lorentzians using Origin-6.1 (Microcal) software. Dispersion curves, velocity as a function of scaling parameter Q∥d, where d is film thickness, were calculated using Mathematica.

3.3 One-dimensionally Confined Nanostructures: Thin Films

Brillouin scattering was used to measure the longitudinal elastic modulus of confined polymers in smooth polystyrene (PS) films (1-D confinement). The PS films were fabricated at the National Institute of Standards and Technology (NIST). Polystyrene (PS, a NIST Standard Reference Material, SRM 705, Mₘ = 179 kg/mol, Mₙ = 171 kg/mol) was dissolved in toluene at various mass fractions and filtered through a 0.45 μm Teflon filter. The solutions were spun cast onto Si wafers primed with hexamethyldisilizane (HMDS), which creates a visibly hydrophilic Si surface. After spin casting, annealing the films for 1 h at 135 °C under vacuum of approximately 5 Pa removed residual toluene. The film thickness after vacuum annealing, measured by NIST using specular X-ray reflectivity, ranged from 1150.0 nm to 358.5 nm.

Brillouin scattering measurements of PS films were performed with ~10-20 mW p-polarization incident on the sample. No spatial filter was used in the incident beam path. The f/2 lens was used as the collecting optics and the small mirror was the backscattering mirror. No analyzer was used for the scattered light. The PS films were
measured at very low $\theta$ to estimate sound velocity from equation 2.18 ($V = 2\Delta \nu d$). The free spectral range of the interferometer was set to 20 GHz, or a mirror spacing of 7.5 mm.

Brillouin scattering was also used to study uniform films of photoresist (PR) polymer and silicon oxide ($\text{SiO}_x$) on Si. The experimental conditions were similar to those of the PS films, but additional polarizations and incident angles were measured. For $\text{SiO}_x$ films on Si, incident power on the sample was higher (~30-90 mW). Also, $\text{SiO}_x$ films were measured using the 10x objective with either the small mirror (including spatial filter) or the semi-transparent mirror (without spatial filter) as the backscattering mirror. Both PR and $\text{SiO}_x$ film measurements were used as a reference for more complex structures and details will be discussed in following sections.

The thickness of the $\text{SiO}_x$ film was estimated from the split of the longitudinally guided acoustic mode and equation 2.18 to be $d(\text{SiO}_x) \sim 990$ nm. The longitudinal sound velocity of $\text{SiO}_x$ was taken to be that of $\text{SiO}_2$ 5.9 km/s.\textsuperscript{177} The split of the LGM in the Brillouin spectra, measured at $Q_{||} = 5.5 \ \mu\text{m}^{-1}$, was $\Delta \nu \sim 3.0$ GHz.

3.4 Two-dimensionally Confined Nanostructures: Grating Lines

Brillouin scattering was used to measure phonon propagation and elastic constants in high aspect ratio photoresist (PR) polymer and silicon oxide ($\text{SiO}_x$) line patterns. Small angle X-ray scattering was used to measure the dimensions of the gratings,\textsuperscript{178} with additional details included in Appendix E.
At low scattering angles, diffraction peaks from the grating samples broadened the elastic line, making it difficult to interpret low frequency Brillouin peaks. It was possible to suppress some of the elastic tail at angles $\theta = 15^\circ - 25^\circ$ using a narrow mask placed over the lens focusing light to the pinhole of the interferometer, as depicted in Figure 48a. With gratings oriented parallel to $Q_{||}$, the mask blocked the diffraction peaks created by the 1 $\mu$m spacings between grating sets. The spectral comparison in Figure 48b shows the effectiveness of the mask in narrowing the elastic line to more clearly reveal low frequency Brillouin peaks.

![Figure 48](image)

Figure 48  (a) Illustration of the mask used to block diffraction peaks from entering the interferometer and (b) low frequency Brillouin spectra from 112 nm gratings (21-5-OX) at $25^\circ$ ($Q_{||} = 10 \mu m^{-1}$) without the mask (thick line) and with the mask (thin line).

3.4.1  Polymer Grating Lines

Two separate sample sets of photoresist gratings were analyzed. For all of the structures, the patterned (gratings) and unpatterned (smooth film) regions on the wafer were measured to compare elastic properties under 2-D and 1-D confinement. For both sets, deep UV lithography was used to fabricate large arrays of parallel photoresist ridges.
(gratings) on a Si wafer. The sample was rotated in the scattering plane to change the incident angle $\theta$ and the magnitude of the wave-vector parallel to the film surface, $Q_{||} = (4\pi \text{Sin}\theta)/\lambda$. The laser spot from the $f/2$ lens had a diameter about 30 $\mu$m, i.e. an area that covered about one hundred ridges of the gratings. Most measurements were performed using $p$-polarization $\sim$10-20 mW on the sample. In some cases, $p-s$ polarization was collected using a polarization analyzer in the scattered beam.

The first set of gratings, from the Shipley Corporation, was fabricated using 248nm lithography. The Shipley gratings were measured for preliminary comparison between Brillouin spectra of films and gratings. The second set of gratings, from IBM, was fabricated using 193 nm lithography. The Brillouin spectra of the IBM gratings were measured more extensively. Scanning electron microscopy (SEM) images in Figure 49 and Figure 50 show the uniformity, aspect ratio, and spacing of representative Shipley and IBM grating samples, respectively.

![Figure 49](image)

Figure 49 Scanning electron micrograph of 180 nm wide polymer lines in the grating sample from Shipley.

The IBM gratings consisted of lithographically patterned arrays of parallel lines (gratings) of a JSR$^{179}$ AR237 photoresist on oxidized Si substrates with an intermediate AR19 bottom antireflective coating (BARC) (Figure 50). The IBM sample set consisted of approximately equal grating lines and spacing (pitch 1:1) with ridge widths varying
from ~130 nm down to ~80 nm (see Table 1). The AR237 PR film thickness (and grating line height) as measured by ellipsometry at NIST was 316 ± 9 nm and the AR19 BARC was 54 ± 10 nm thick. A layer of unpatterned photoresist film and BARC existed on the margins and between patterned regions, with total thickness, \((h+d) = 370 ± 20 \text{ nm}.

![Figure 50 SEM cross-section of photoresist (PR) gratings (JSR AR237) from IBM showing the PR height \((h \sim 320 \text{ nm})\), the BARC thickness \((d \sim 50 \text{ nm})\), and the top of the SiO\(_x\) substrate (1 \(\mu\)m thick on a Si wafer). The PR width of each sample was uniform within a 4 mm square, with squares ranging from \(w = 81 – 126 \text{ nm}\).](image)

The IBM samples were square-shaped silicon wafers, with 16 small (4x4 mm) patterned regions. They were labeled in the style \textit{Dose Number-Row number-Material}, referencing the sample’s position from the original 200 mm wafer. The mask/wafer layout is attached as Appendix F. Within a single sample, each 4 mm square contained a pitch and feature size, as depicted in Appendix G “The proposed binary mask for 0.68NA 193 nm ASML Tool”. The actual pitches and feature sizes varied from the proposed sizes depending on dose number (mJ/cm\(^2\)), as shown in Table 1 by the table and plot of Line Width vs. Exposure Dose in Appendix E.

The specifications of the measured JSR grating samples, with ridge widths ranging from 81nm to 126nm, are listed in Table 1. The gratings with widths \(w\) of 88 nm (24-3-PR 110) and 126 nm (21-5-PR 150) were studied most thoroughly, indicated in
bold in Table 1. The pitches of square labels 110, 120, and 150 were 216 nm, 235 nm, and 294 nm, respectively.

Table 1: IBM grating samples measured using Brillouin light scattering. Bold type indicates samples measured thoroughly to quantify elastic properties.

<table>
<thead>
<tr>
<th>Sample Label</th>
<th>Square Label</th>
<th>Actual Linewidth (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21-3-PR</td>
<td>1:1; 120</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>126</td>
</tr>
<tr>
<td>21-5-PR</td>
<td>1:1; 120</td>
<td>105</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>126</td>
</tr>
<tr>
<td>23-1-PR</td>
<td>1:1; 110</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td>1:1; 120</td>
<td>97</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>120</td>
</tr>
<tr>
<td>24-3-PR</td>
<td>1:1; 110</td>
<td>88</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>117</td>
</tr>
<tr>
<td>25-3-PR</td>
<td>1:1; 110</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>113</td>
</tr>
<tr>
<td>25-5-PR</td>
<td>1:1; 120</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>1:1; 150</td>
<td>113</td>
</tr>
<tr>
<td>21-5-Ox</td>
<td>1:1; 150</td>
<td>148</td>
</tr>
<tr>
<td></td>
<td>1:1; 112</td>
<td>112</td>
</tr>
</tbody>
</table>

Typically, the most visually prominent squares were those in the corner with pitch 1:1 and feature sizes of 110, 120, and 150 nm. Within each 4 mm square, line features were 10 µm in length and grouped in sets with film spacings 1 µm wide, as shown in Appendix H “Within Each 4 mm Square”. The 1µm spacing perpendicular to the grating lines created a diffraction pattern that provided a means to check the orientation of the gratings. For example, if the diffraction peaks from the spacings lay in the horizontal plane, the gratings were also oriented horizontally.

To meet the necessary conditions for equation 2.18 for calculating longitudinal sound velocity, measurements were performed at a small angle of θ = 8° (Q|| = 3.4 µm⁻¹). The diffracted light from the grating at low Q|| caused a broad elastic tail in the Brillouin
spectra of gratings oriented parallel to $Q_{||}$, prohibiting analysis of low-frequency modes for data collected at $\theta = 8^\circ$. The peaks at $Q_{||} = 3.4 \, \mu m^{-1}$ remained below the elastic tail, even with a narrow mask as in Figure 48a.

The unpatterned photoresist film, also referred to as the ‘margin’, was measured for a reference. BLS spectra for grating widths 88 nm and 126 nm were measured at six angles $\theta$ (15\(^\circ\), 25\(^\circ\), 35\(^\circ\), 45\(^\circ\), 55\(^\circ\), and 67\(^\circ\)). The range of $Q_{||}$ values and scaling parameters for surface wave analysis are listed in Table 2.

Table 2  Experimental angles and corresponding scaling parameters for Brillouin measurements of PR gratings

| Angle ($^\circ$) | $Q_{||}$ ($\mu m^{-1}$) | $Q_{||}$ 370 nm PR Film | $Q_{||}$ 88 nm PR Gratings | $Q_{||}$ 126 nm PR Gratings | $Q_{||}$ 112 nm OX Gratings | $Q_{||}$ 148 nm OX Gratings |
|------------------|------------------------|------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 8                | 3.4                    | 1.26                   | 0.30                      | 0.43                      | N/A                       | N/A                       |
| 15               | 6.32                   | 2.34                   | 0.56                      | 0.80                      | 0.71                      | 0.94                      |
| 25               | 10.32                  | 3.82                   | 0.91                      | 1.30                      | 1.16                      | 1.53                      |
| 35               | 14.01                  | 5.18                   | 1.23                      | 1.77                      | 1.57                      | 2.07                      |
| 45               | 17.27                  | 6.39                   | 1.52                      | 2.18                      | 1.93                      | 2.56                      |
| 55               | 20.01                  | 7.40                   | 1.76                      | 2.52                      | 2.24                      | 2.96                      |
| 67               | 22.48                  | 8.32                   | 1.98                      | 2.83                      | 2.52                      | 3.33                      |

3.4.2  Silicon Oxide Grating Lines

Silicon oxide gratings were measured under similar conditions to silicon oxide films, or margins, as described in Section 3.3. A frequency lock box was not used for the silicon oxide gratings measurements with a semi-transparent mirror, therefore the elastic line was slightly broadened making low frequency modes harder to distinguish. The free spectral range of the interferometer was set to 20, 50, or 72 GHz. The sample 21-5-OX
was measured at angles listed in Table 2 between \( \theta = 35^\circ - 67^\circ \), or \( Q_\parallel = 14 \ \mu m^{-1} - 22.5 \ \mu m^{-1} \). Thorough studies were conducted for 21-5-OX film (margin), 150, and 110 nm structures as indicated in bold in Table 1.

Brillouin spectra were collected for SiO\(_x\) gratings oriented parallel (horizontally) and perpendicular (vertically) to \( Q_\parallel \) with incident \( p \)- and \( s \)-polarization. In some cases a polarization analyzer was used for the scattered light, to measure spectra using \( p-s \) polarization.

Two separate data sets were collected from two experimental setups. The first set used the 10x Mitutoyo objective and the small mirror. As discussed in Section 3.2, the blocked signal from the small mirror distorts the absolute frequencies of the data, but this data set was effective for comparing spectral effects of polarization and grating orientation. The second set used the 10x objective and the semi-transparent mirror. The absolute frequencies from the second set agreed with theoretical predictions. However, the signal intensity and spectral resolution were inferior to the first set, making this data less practical for determining effects from polarization and grating orientation.

The intensity of \( s \)-polarized light reflected from the semi-transparent mirror, and thus incident on the sample, was almost 3 times higher compared to \( p \)-polarized light. Besides higher signal intensity, \( s \)-polarization yielded different spectral features than \( p \)-polarization that will be discussed in Chapter V.
3.5 Three-dimensionally Confined Nanostructures: Spheres

Brillouin scattering was used to measure assemblies of poly(methyl methacrylate) (PMMA) spheres and Wiseana Iridovirus (WIV) particles. Spherical particles of PMMA or WIV on aluminum or silicon substrates were prepared using convective assembly at the Air Force Research Laboratory (AFRL) by Stephen Wargacki, as illustrated in Figure 51.

Figure 51 Schematic of convective assembly of particles (PMMA or WIV) in solution onto a substrate (from Stephen Wargacki).

The rate of assembly \( v_w \) controlled the thickness, or surface coverage, of the nanospheres on the Si. The samples were stored and measured at temperatures between 19-24°C and relative humidity’s between 10-30%.

Brillouin measurements of the PMMA and WIV assemblies were performed using \(~10-30\) mW laser power and \( s \)-polarization incident on the sample. No spatial filter was used in the incident beam. The semi-transparent mirror and 10x Mitutoyo objective were the focusing aperture and backscattering mirror, respectively. The laser spot size was about 10 \( \mu \text{m} \). The free spectral range of the interferometer was set to 30, 50, or 72 GHz. Samples were measured at angles \( \theta = 35^\circ - 75^\circ \), or \( Q_{\parallel} = 14 \mu \text{m}^{-1} - 24 \mu \text{m}^{-1} \).
3.5.1 Polymer Spheres

The 300nm diameter PMMA spheres (Polysciences, Inc.) were used as received (2.55% solids in water). Assembly occurred at a rate of 10 µm/s at 23°C and at 15% R.H.

Figure 52 Scanning electron micrograph of PMMA (D = 300nm) on an Al mirror.

3.5.2 Wiseana Iridoviruses

Wiseana Iridovirus is a double-stranded deoxyribonucleic acid (ds-DNA) virus that infects larvae. A transmission electron microscopy (TEM) image of WIV single virus particles (Figure 53a) shows the ds-DNA core surrounded by a lipid bi-layer and capsid shell. The total diameter of an icosahedral (nearly spherical) WIV virion is ~ 140 nm, with the average thickness of the proteinaceous shell ~ 4 nm.
Films and surface coverages of WIV were prepared on aluminum mirrors and silicon substrates to reduce the spectral overlap between the Rayleigh line from the substrate and WIV. Increasing the rate of convective assembly by 10 times compared to the deposition of multi-layer coverage generated single layer films (Figure 53c and d). Diluting the virus solution and increasing the convective assembly rate by another 10 times generated sub-monolayer films (Figure 53b). All films were imaged using a FEI XL30 Scanning Electron Microscope at AFRL using 3 kV at a distance of 5 mm.

WIV layers on aluminum mirrors were measured in a custom-built humidity chamber. The chamber consisted of a Proteus Industries Inc. fluid flow switch with four valve openings. Three of the four valves were sealed with Teflon tape covered screws. A tube connected a reservoir to the sealed chamber in a closed loop system. The reservoir contained distilled water for 100% relative humidity (R.H.) and dessicant chips for dry (<10%) R.H. It was also possible to place various salt mixtures to obtain intermediate
Glass was used to cover the front of the chamber. Initially, a thick glass microscope slide (thickness ~ 1 mm) was glued with epoxy to the front of the fluid flow cell. It was not possible to obtain a Brillouin signal from the virus samples with this thick glass as the front window of the cell. A thinner (thickness ~0.1mm) cover slip did not interfere with the Brillouin peak intensity or frequency. The chamber is pictured in the light scattering setup in Figure 54. Notice the bulky geometry of the chamber limited measurements with the long-working Mitutoyo objective to a maximum angle of $\theta = 50^\circ$ ($Q_\parallel = 18.7 \, \mu m^{-1}$).

Figure 54 The custom-built humidity control chamber, secured to the goniometer in the light scattering setup.

Humidity effects on Brillouin spectra are discussed in Chapter IV followed by a detailed analysis of WIV vibrational spectra and estimates of mechanical properties.
CHAPTER IV

VIBRATIONS AND MECHANICS OF POLYMERIC NANOSTRUCTURES

This chapter describes the application of Brillouin spectroscopy to polymeric structures with spatial confinement in one-dimension (thin films), two-dimensions (grating lines), and three-dimensions (spheres).

4.1 Polystyrene Thin Films

The Brillouin spectra from bulk polystyrene (PS) and PS films with thicknesses 1150 nm, 688 nm, and 359 nm, measured at low $Q_{||} = 3.4 \mu m^{-1}$ are shown in Figure 55. The split of the longitudinal mode increased with decreasing thickness, as expected for guided modes resulting from confinement dimensions on the order of $\lambda_{ph} \sim 2\pi Q_{||}$ or less.
Figure 55 Brillouin spectra of bulk PS and PS films on silicon as a function of film thickness measured at $Q_{||} = 3.4 \, \mu m^{-1}$ ($\theta = 8^\circ$).

Analysis of the frequency split $\Delta \nu$ of the longitudinal guided modes (LGM) using equation 2.18 shows that the longitudinal sound velocity does not vary with the PS thickness (at least to within 3%) in films down to $d \sim 360$ nm (Figure 56).

Figure 56 The longitudinal sound velocity estimated from the split energy as a function of the PS film thickness.
This result is not surprising because the film thickness is much greater than the molecular dimensions. Further, $V_L$ agrees with studies on free-standing PS films where variations were not observed even down to $d = 29 \text{ nm}^{76}$ and supported (multi-layer) films down to 16 nm.$^{75}$ The average value of $V_L = 2.32 \pm 0.02 \text{ km/s}$, assuming $\rho = 1.056 \text{ g/cm}^3$, yields $c_{ll} = 5.68 \pm 0.10 \text{ GPa}$ and is also in agreement with previous Brillouin studies of unsupported and supported PS films.$^{69,76}$

At this low $Q_{||}$, the frequency of the lowest frequency surface mode, the Rayleigh mode, was too low to be analyzed. Measurements and analysis of phonons in photoresist films will be discussed in the next section for direct comparison with grating structures.

4.2 Photoresist Gratings

Gratings from the Shipley Corporation provided the first insight into phonon propagation in periodic polymeric grating lines. Gratings from IBM were studied more thoroughly for deriving elastic moduli from the phononics of the photoresist lines.

4.2.1 Shipley Gratings

Back-scattering measurements of the Shipley photoresist film at low $Q_{||}$ ($Q_{||} = 3.4 \mu\text{m}^{-1}$, $\theta = 8^\circ$) (Figure 57, thick line) gave a split of the LGM peaks of $\Delta \nu \sim 2.95 \text{ GHz}$. With film thickness of approximately 360 nm, equation 2.18 yielded a longitudinal sound
velocity ~ 2.1 km/s. The LGM peaks from the grating lines with 180 nm width were broad and convoluted (Figure 57, thin line), making it difficult to estimate $\Delta \nu$.

![Brillouin spectra of the Shipley photoresist film (thick) and 180 nm gratings (thin) measured at $Q_{||} = 3.4 \mu m^{-1}$](image)

Figure 57  Brillouin spectra of the Shipley photoresist film (thick) and 180 nm gratings (thin) measured at $Q_{||} = 3.4 \mu m^{-1}$.

The spectra from the Shipley photoresists measured at higher angles ($Q_{||} = 22.5 \mu m^{-1}$), as in Figure 58, display sharp Rayleigh modes. The Rayleigh mode is nearly the same in the film and the grating, both in frequency and width, giving estimates of $V_R$(film) = 1.21 ± 0.02 km/s and $V_R$(180 nm) = 1.24 ± 0.02 km/s. Therefore, shear modulus, related to the Rayleigh velocity, of the Shipley gratings remained the same as in the unpatterned Shipley film. The narrow linewidth suggests a long phonon lifetime, indicative of Rayleigh surface waves.$^{128}$
Figure 58  Brillouin spectra of the Shipley photoresist film (thick line), 180nm grating with ridges parallel to $Q_{||}$ (thin line), and 180 nm grating with ridges $\perp$ to $Q_{||}$ (dashed line). The spectra were measured at $\theta = 67^\circ$ ($Q_{||} = 22.5 \ \mu m^{-1}$) and the Rayleigh mode is indicated ($R$). Brillouin modes in the Shipley gratings were suppressed if the gratings were oriented perpendicular to $Q_{||}$.

Preliminary measurements of the Shipley gratings indicated that the Brillouin spectrum depended strongly on orientation of the gratings relative to $Q_{||}$. In these initial measurements, all Brillouin modes in spectra measured at high $Q_{||}$ perpendicular to the grating ridges were suppressed (Figure 58, dotted line), indicating an absence of phonons propagating across the gratings. Apparently, phonon propagation in the Shipley gratings mainly occurred along the long axes of the grating ridges and not across the ridges. Further, no localized ($Q_{||}$ independent) vibrations of the grating lines were observed.

4.2.2 IBM Gratings

Grating patterns from IBM were studied in more detail than the Shipley gratings because i) dimensions were smaller and more numerous (more than 10 widths between
81 and 126 nm compared to widths > 180 nm), ii) the dimensions were better characterized by NIST (Appendix E), and iii) their pattern quality was apparently better. The better pattern quality, as suggested by critical dimension small angle x-ray scattering,\textsuperscript{178} may have led to more distinct modes in the IBM gratings (Figure 59) than the Shipley gratings (Figure 58). The Brillouin spectra for the IBM photoresist films at $Q_{\parallel} = 3.4 \ \mu m^{-1}$ revealed a few LGM peaks with frequency split $\Delta \nu = 3.25 \pm 0.10$ GHz (Figure 59). At low $Q_{\parallel}$, equation 2.18 yields a valid estimate for longitudinal sound velocity of the photoresist polymer from $\Delta \nu$. The film thickness was taken from the SEM images (Figure 3.10) and ellipsometry data from NIST as the feature height plus the BARC layer, $(h+d) = 370 \pm 20$ nm. This total thickness $(h+d)$ yielded an estimate of the longitudinal sound velocity using the relation $V_L = 2(h+d)\Delta \nu = 2.4 \pm 0.2$ km/s.

Notice the frequency of the main LGM peak near 12 GHz remains unchanged (dashed line, Figure 59), within approximately 3%, for the spectra of the 126 nm and 88 nm gratings measured under identical conditions as the film. The unchanging frequency from film to gratings indicates that the longitudinal velocity, and thus longitudinal modulus, does not change for structures confined to dimensions as low as 88 nm. The LGM peaks from the gratings are broadened in comparison to the unpatterned film, likely due to damping of the modes confined in the ridges. Strong scattering of phonons on the side surfaces of the ridges may be one reason for the increased damping. If the single confining dimension of a thin film creates discrete guided phonons, then an additional confining dimension introduced by the grating sidewalls likely creates additional allowable phonons. Although the broadening makes interpretation of $\Delta \nu$ difficult, the
unchanging central frequency is still a good indicator that the modulus is also unchanging.

![Brillouin spectra](image)

Figure 59  Brillouin spectra of the resist films and 21-5-PR 150 and 24-3-PR 110 gratings with ridge widths 126 nm and 88 nm, respectively. Spectra were measured at $Q_{||} = 3.4 \mu m^{-1}$ ($\theta = 8^\circ$) and the ridges aligned parallel to $Q_{||}$. New modes not present in the unpatterned film appear in the spectra of the gratings in the frequency range between 6 GHz and 10 GHz.

Rotating the surface normal relative to the incident light, i.e. increasing $Q_{||}$, reveals the propagating nature of the surface phonons (Figure 60). As expected, the Rayleigh mode, the principle film-guided wave at the film surface, was typically the most intense Brillouin peak in both film and gratings spectra. Peaks at higher frequencies arose from higher-order surface (Sezawa) waves in the film or analogous modes in the grating lines.
Figure 60  Brillouin spectra of the IBM resist film and gratings measured at $Q_{\parallel} = 22.5 \ \mu m^{-1}$ ($\theta = 67^\circ$) with orientation of ridges parallel to $Q_{\parallel}$. The Rayleigh mode is indicated with the vertical dashed line.

The fit of $\nu_R = 4.29 \pm 0.05$ GHz at $Q_{\parallel} = 22.5 \ \mu m^{-1}$ gave an estimate for Rayleigh velocity for the film, $V_R = 1.20 \pm 0.02$ km/s. At $Q_{\parallel}(h+d) \sim 8.3$, this Rayleigh velocity reflects the elasticity of the photoresist and not the underlying substrate. From equation 2.34, transverse velocity of the PR film and gratings can be estimated as $V_T = 1.30 \pm 0.03$ km/s (Mathematica code in Appendix B). Figure 61 shows the frequency of the Rayleigh mode measured in a few grating structures and in the film (dashed line). No variation in the Rayleigh frequency, $\nu_R$, was observed for ridges with widths as narrow as 81 nm. Uncertainties of the frequency are estimated from averaging the Stokes and anti-Stokes Rayleigh modes and uncertainty of the angle $\theta (\pm 1^\circ)$. 
The absence of significant variations in $V_R$ (Figure 60, Figure 61) between the film and gratings indicates that the shear elastic modulus is the same in the smooth films and the patterned features. Apparently, the formation of narrow ridges with widths down to 88 nm does not affect shear (G) or longitudinal (M) moduli of the photoresist along the polymeric lines.

4.2.2.1 Brillouin Modes of Photoresist Gratings Oriented Perpendicular to $Q_{||}$

Figure 62 shows representative spectra of the IBM photoresist film (thick line) and 88 nm gratings oriented parallel (dashed line) and perpendicular (thin line) to $Q_{||} = 22.5 \ \mu m^{-1}$. Contrary to the Shipley gratings, Brillouin modes were observed in IBM gratings oriented perpendicular to $Q_{||}$, that is vertically oriented gratings.
Figure 62. Brillouin spectra of the 24-3-PR IBM photoresist film (thick line), and 88 nm grating with grating lines parallel (dashed line) and perpendicular (thin line) to $Q_{||}$ measured at $Q_{||} = 22.5 \mu m^{-1}$ ($\theta = 67^\circ$). The Rayleigh mode is indicated ($R$). Brillouin modes in the IBM gratings were not completely suppressed if the gratings were oriented perpendicular to $Q_{||}$. The spectra are shifted vertically for visual clarity.

The exact material differences between Shipley and IBM gratings are unknown, but the grating patterns are certainly different. Namely, the IBM samples contained 1 $\mu$m stripes spaced apart by 10 $\mu$m, and the Shipley gratings did not. When the IBM gratings were perpendicular to $Q_{||}$, these 1 $\mu$m wide stripes between grating sets were parallel to $Q_{||}$ (see Appendix H). The illumination area of the incident beam was $\sim$10 $\mu$m (with 10x objective), so scattering should have occurred from at least 1-2 stripes. The Brillouin spectrum from these stripes should be similar to that from the unpatterned film, but this does not seem to be the case for most $Q_{||}$. Notice in Figure 62 the Brillouin modes from gratings perpendicular to $Q_{||}$ do not appear at the same frequency as modes propagating along the gratings, except perhaps the Rayleigh mode which might be a coincidence as shown by the analysis below. The differences in frequencies between grating orientations
indicate the modes observed from gratings oriented perpendicular to $Q_\parallel$ have a different nature or travel through a different medium than the parallel gratings or the film.

The nature of some of the modes in spectra from IBM gratings oriented perpendicular to $Q_\parallel$ can be inferred from their dependence on $Q_\parallel$. Figure 63 contains Brillouin spectra from a wide range of $Q_\parallel$ for the IBM PR gratings oriented perpendicular to $Q_\parallel$. Figure 64 plots the low frequency mode for these data sets.

![88 nm PR Vertical Gratings](image)

Figure 63 Comparison of Brillouin spectra from 88 nm gratings at various $Q_\parallel$ with gratings oriented perpendicular (vertical) to $Q_\parallel$. The dashed lines indicate the $Q_\parallel$-independent modes.
Figure 64 Lowest frequency $Q_{\parallel}$ independent Brillouin mode observed for 88 nm PR gratings oriented perpendicular to $Q_{\parallel}$ (vertically oriented gratings).

Notice from Figure 63 and Figure 64 the $Q_{\parallel}$ independent modes at $\nu = 1.54 \pm 0.02$, $3.3 \pm 0.1$, and $7.2 \pm 0.1$ GHz. These frequencies are labeled with dashed lines in Figure 63 and in the frequency dispersion plot in Figure 65.

![Figure 64](image.png)

Figure 65 Frequency dispersion of Brillouin modes observed when the 88 nm IBM PR grating lines were oriented perpendicular to $Q_{\parallel}$. The $Q_{\parallel}$ independent, possibly localized modes, are indicated by the dashed lines. The dimensions associated with each localized mode frequency are listed as calculated from the $V_L = 2.4$ km/s and $V_T = 1.3$ km/s of the PR film.

![Figure 65](image.png)
$Q_{\parallel}$ independence indicates the vibrations are non-propagating and the Brillouin modes from gratings perpendicular to $Q_{\parallel}$ are from localized resonances of the polymeric lines. At first approximation, the lowest frequency resonances within a beam satisfy the conditions in which the confining dimension $D_c = \lambda_r/2$, where $\lambda_r$ is the resonant wavelength within the confined structure. Sound velocity associated with such a resonance follows the relationship $V_i = \lambda_r \nu$, where the subscript $i$ denotes longitudinal or transverse velocity depending on the nature of the resonance. Substituting, the confining dimension can be estimated from $D_c = V_i/2\nu$.

The mode at $7.2 \pm 0.2$ GHz, if associated with transverse sound velocity $V_T = 1.3 \pm 0.05$ km/s, yields a confining dimension of $90 \pm 5$ nm, within the range of the grating width. So, this might be a shear mode of the lines subject to the same elasticity as the bulk photoresist and film. The mode at $3.3 \pm 0.1$ GHz seems to be associated with a longitudinal resonance of the grating line height, yielding $D_c = 360 \pm 40$ nm from $V_L = 2.4 \pm 0.2$ km/s in the lines that are $316 \pm 9$ nm tall with a $54 \pm 10$ nm underlying BARC. If indeed these two $Q_{\parallel}$ independent modes are related to the localized shear resonance of the width and longitudinal resonance of the height, first approximations suggest that sound velocities are similar to those of the bulk. However, the mode at $1.54 \pm 0.02$ GHz yields $D_c = 420 \pm 20$ nm for a transverse velocity $V_T = 1.30 \pm 0.05$ GHz. It seems unlikely this lowest frequency $Q_{\parallel}$ mode is a shear resonance associated with the height because this would suggest that the shear modulus decreases in the height direction (370 nm feature) but not the width direction (88 nm feature). Additionally, it is unreasonable to assign this mode to a longitudinal resonance of almost 800 nm because such a dimension is well above any fundamental dimensions of the grating lines. The $Q_{\parallel}$
independent modes, in addition to the unidentifiable $Q_{\parallel}$ dependent modes in Figure 65, make it difficult to extract a full interpretation of the phonon spectra for the purposes of calculating elastic moduli.

Previous measurements of periodic structures, shallow Si grooves oriented perpendicular to $Q_{\parallel}$, revealed a mixing (hybridization) of Rayleigh waves and longitudinal waves of the bulk Si.$^{112,113,114,115}$ Also observed in those studies were Brillouin zone-folded surface acoustic modes associated with the gratings, in which phononic band gaps existed at wavevectors $Q = m\pi/\Lambda_G$, where $m$ are integers and $\Lambda_G$ was the pitch of the periodic features. Neither evidences for zone-folding nor phononic band gaps were observed for the high-aspect ratio photoresist gratings on SiO$_x$ studied here.

4.2.2.2 Brillouin Modes Unique to Gratings Oriented Parallel to $Q_{\parallel}$

Brillouin modes observed propagating parallel to the gratings were studied more carefully for their implications to elastic properties of the polymeric nanolines. Phonons observed in the film and along the grating lines allowed direct comparison of sound velocities and elastic moduli. In general, the Brillouin spectrum of gratings parallel to $Q_{\parallel}$ was richer than that from a simple unpatterned film. As compared to the film spectra, the gratings spectra contain new modes, none of which were anticipated or predicted by any existing theory. The observed broadening of the LGM modes and appearance of new modes seem to be general features for the Brillouin spectra of sub-micrometer polymeric gratings.
The first set of additional modes in gratings oriented parallel to $Q_||$ appear between 5 GHz and 10 GHz, where intense modes are not seen in the unpatterned regions of the film (Figure 59). As seen in Figure 66, the frequencies of these modes are width dependent.

![Graph showing Brillouin spectra at $Q_|| = 3.4 \, \mu m^{-1}$ from 23-1-PR 110, 120, and 150 with actual linewidths of 90 nm (dashed line), 97 nm (thin line), and 120 nm (thick line), respectively.]

Figure 66  Brillouin spectra at $Q_|| = 3.4 \, \mu m^{-1}$ from 23-1-PR 110, 120, and 150 with actual linewidths of 90 nm (dashed line), 97 nm (thin line), and 120 nm (thick line), respectively.

Additionally, the average frequency split between these additional modes increases with decreasing ridge width (Figure 67). Further quantitative analysis did not reveal clear sound velocity information from these propagating modes, but the qualitative frequency and frequency split dependencies on grating width clearly indicates some type of a lateral confinement within the grating lines.
Figure 67 Frequency splits between the additional Brillouin modes (between 5 GHz and 10 GHz as in Figure 59 and Figure 66) in a series of IBM gratings as a function of the ridge width in the gratings measured at $Q_{||} = 3.4 \ \mu m^{-1}$.

Another unexpected mode appeared at frequencies below the Rayleigh mode and was naively termed the sub-Rayleigh (sub-R) mode. Recall that no modes are expected at frequencies below the Rayleigh mode in Brillouin spectra for a damping supported film system. In a Brillouin study of silicon oxynitride films grown on gallium arsenide, a shear horizontal mode was observed with a frequency below the Rayleigh frequency of the films. In that study, the mode was assigned to a soft, thin transition layer between the film and substrate. Although the IBM photoresist samples studied here have a 50 nm BARC layer, the sub-R mode does not appear in the film spectra and thus has an origin specific to the gratings. In fact, the absence of a low-frequency mode in the film supports the assumption that the BARC and the photoresist have similar elastic properties. Thus, the BARC layer was ruled out as the origin of the sub-R mode.
Interpretation of the sub-\(R\) mode required a more detailed study of phonon propagation in the grating structures, including analysis of the dispersion relationship and polarization dependence. For this, IBM gratings with the widths 126nm (21-5-PR 150) and 88nm (24-3-PR 110) were measured most thoroughly, for 3.4 \(\mu m^{-1} \leq Q_\parallel \leq 23 \mu m^{-1}\), for comparison with the unpatterned film. Figure 68 and Figure 69 illustrate the \(Q_\parallel\) dependence of the surface Brillouin modes of the 88 nm and 126 nm IBM photoresist gratings, respectively.

![Figure 68](image_url)  
**Figure 68**  Brillouin spectra from 88 nm IBM 24-3-PR gratings oriented parallel to \(Q_\parallel\) at various \(Q_\parallel\).
The frequency of the sub-$R$ mode depended on grating width $w$, illustrated by Figure 70b and Figure 70c. The sub-$R$ mode appeared in spectra from the grating samples but not from uniform films, suggesting that displacements were confined within the grating lines. Notice also the sub-$R$ mode is the only mode that appears in depolarized scattering ($p$-$s$ polarization) spectra from the gratings (Figure 70d and Figure 70e). In supported films, only shear horizontal waves appear in Brillouin scattering under $p$-$s$ polarization conditions. The displacements of shear horizontal waves are in the surface plane, causing them to rotate $p$-polarization to $s$-polarization upon scattering. The shear horizontal nature of the sub-$R$ mode indicates it is associated with displacements perpendicular to the side surfaces of the grating lines.
Figure 70 Brillouin scattering spectra at $Q_{||} = 22.5 \, \mu m^{-1}$ ($\theta = 67^\circ$) of the IBM photoresist (a) film, (b) 88 nm gratings and (c) 126 nm gratings without polarization analyzer. Depolarized ($p$-$s$ polarization) spectra of (d) 88 nm gratings and (e) 126 nm gratings oriented parallel to $Q_{||}$. Peaks from Rayleigh (R), sub-Rayleigh ($sub$-$R$) and Sezawa ($S$) modes are labeled.

To extract elastic properties from the $sub$-$R$ mode, analysis of its dispersion relationship and comparison with theory was required. Dispersion pertains to the $Q_{||}$-dependence of the frequency or velocity of the mode. The frequency dispersions of the sub-Rayleigh, Rayleigh, and first two Sezawa modes are plotted in Figure 71 with dispersion curves calculated by Dr. Colm Flannery at NIST, Boulder. In general, the surface Brillouin modes observed for the film and both grating widths can be described by the same set of dispersion curves, or elastic constants, further indicating no change in modulus associated with these phonon displacements. However, the dispersions of the
sub-Rayleigh mode from both grating widths do not follow the same relationship when scaled to $Q_{\parallel}(h+d)$. More detailed analysis based on phonon velocity was performed using the velocity dispersion relationships expressed in the matrix equation 2.29.

Figure 71  Frequency dispersion of the Brillouin modes from the IBM PR film (squares), 126 nm gratings (triangles) and 88 nm gratings (circles) scaled to $Q_{\parallel}(h+d)$. The lines represent calculated dispersions.

As discussed in Chapter II, Brillouin surface modes can be analyzed in terms of the dispersion of the sound velocity $V$ calculated from the mode frequency,$^{128}$

$$V = \frac{2\pi \nu}{Q_{\parallel}} = \frac{\nu \lambda_0}{2 \sin \theta},$$

(4.1)

where $Q_{\parallel} = 4 \pi \sin \theta \lambda$ is the scattering wave vector parallel to the plane of the film, and $\lambda_0$ is the wavelength of incident light (514.5 nm). The velocities of the sub-Rayleigh, Rayleigh, and first Sezawa peak from the IBM photoresist film, 126 nm, and 88 nm gratings are plotted in Figure 72 as a function of $Q_{\parallel}(h+d)$. If not visible, experimental error is within the size of the symbols.
Figure 72  Velocity dispersion plots scaled to $Q||(h+d)$, including data from the IBM photoresist film (solid squares), 126 nm gratings (hollow triangles), and 88 nm gratings (hollow circles). The sub-Rayleigh modes are also shown for 126 nm (hollow stars) and 88 nm (solid stars) gratings. The solid lines are calculated dispersion curves for a supported film with $V_L = 2.4$ km/s and $V_T = 1.3$ km/s on a silicon oxide substrate.

Well-established theory of surface waves in thin films provides relationships between the velocities and wave vectors in terms of the density $\rho$, longitudinal $V_L$ and transverse $V_T$ velocities of the film and the corresponding quantities of the substrate, $\rho_{SiO_x}$, $V_{L,SiO_x}$ and $V_{T,SiO_x}$.\textsuperscript{130} A Mathematica program was written to find roots to the matrix equation 2.29, included as Appendix A. For each value of $Q||(h+d)$, the roots of the matrix represent the eigenvelocities present in the film. The dispersion calculations for a photoresist supported film, with parameters as listed in Table 3, are displayed as solid lines in Figure 72.

The photoresist and BARC layer rest on a silicon oxide ($SiO_x$) substrate approximately 1 µm thick on a silicon wafer. To simplify calculations of dispersion
curves, the substrate was approximated as semi-infinite silica (SiO$_2$). The material properties of SiO$_x$ (SiO$_2$) and those calculated for the photoresist layer are listed in Table 3.

Table 3  Physical constants of silicon oxide and photoresist polymer used in the calculations of dispersion curves in Figure 72.

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm$^3$)</th>
<th>$V_L$ (km/s)</th>
<th>$V_T$ (km/s)</th>
<th>$V_R$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_x^{17,18,3}$</td>
<td>$\rho_{SiO_x} = 2.2$</td>
<td>$V_{L, SiO_x} = 5.95$</td>
<td>$V_{T, SiO_x} = 3.74$</td>
<td>$V_{R, SiO_x} = 3.39$</td>
</tr>
<tr>
<td>Photoresist (IBM)</td>
<td>$\rho \sim 1.056$</td>
<td>$V_L = 2.4 \pm 0.2$</td>
<td>$V_T = 1.30 \pm 0.05$</td>
<td>$V_R = 1.20 \pm 0.04$</td>
</tr>
</tbody>
</table>

$V_L$ was estimated from the frequency split, $\Delta \nu = 3.25 \pm 0.10$ GHz of the longitudinal-guided Brillouin peaks of the unpatterned film at $Q_{\parallel} = 3.4 \ \mu$m$^{-1}$ ($\theta = 8^\circ$). The asymptotic Rayleigh velocity, measured at high $Q_{\parallel}(h+d)$ and calculated from $\nu_R = 4.29 \pm 0.10$ GHz, was $V_R = 1.20 \pm 0.04$ km/s. Since amorphous polymers typically have very similar densities, the undetermined density of the resist is taken to be that of polystyrene, 1.056 g/cm$^3$. With $V_L$, $\rho$, $V_{L, SiO_x}$, $V_{T, SiO_x}$, and $\rho_{SiO_x}$ at fixed values, $V_T$ was estimated, $V_T = 1.30 \pm 0.05$ km/s.

Dr. Colm Flannery at NIST calculated the sensitivity of Lamb, Rayleigh, and Sezawa wave velocities to elastic constants for the photoresist film on SiO$_x$. Varying individual parameters including $V_T$, $V_L$, density, thickness, and Poisson’s ratio, he determined the effect of each parameter on the mode velocity as a function of $Q_{\parallel}d$. These calculations indicated that for higher $Q_{\parallel}$, Rayleigh mode velocity is much more sensitive to variations in $V_T$ than in $V_L$, and has very little sensitivity to density. Additionally, dependence on thickness falls off rapidly as the phonon wavelength becomes smaller than the film thickness. For higher order modes, density has a very small effect on Sezawa velocities, while sensitivity to thickness remains significant even...
at high $Q_{ld}$ and $V_L$ is generally less significant than $V_T$. In general, density minimally affects surface wave velocities in this system, which justifies the approximation that density was equal to that of polystyrene. Further, the relatively high sensitivity to $V_T$ compared to $V_L$ and Poisson’s ratio makes estimates of $V_T$ accurate to within the uncertainty of Rayleigh velocity.

It is clear in Figure 72 that the corresponding dispersion curves for the Rayleigh (R) and Sezawa (S) modes adequately describe the Brillouin data for both the uniform film thickness and gratings height of $(h+d)$. Thus, the velocities of the Rayleigh and Sezawa modes are identical in the film and the gratings, regardless of the grating width, and stiffen significantly at small $Q_{\parallel}$ (Figure 72). This is consistent with theory predicting that $V$ increases towards the substrate velocity as the phonon wavelength ($\lambda_{ph} = 2\pi Q_{\parallel}$) becomes larger than the film thickness.

In contrast to this behavior, $V$ of the sub-Rayleigh mode decreases at low $Q_{\parallel}$ (Figure 72). Furthermore, also seen in Figure 70, the sub-Rayleigh frequency is width dependent and appears under depolarized scattering conditions. The peculiar dispersion of the sub-Rayleigh mode, that is decreasing velocity as $Qd$ approaches zero, is similar to the dispersion expected for the lowest-order flexural mode (Lamb wave) of a simple free-standing, or unsupported film. These observations are strong evidence that the sub-Rayleigh mode is a Lamb wave with displacements perpendicular to the grating ridge sidewalls. Essentially, the 320 nm tall structures may have plate modes where the effective plate thickness is equal to the width of the grating ridge.

Rescaling the dispersion of the sub-$R$ modes to the width $w$ of the structures (Figure 73), instead of $(h+d)$ as in Figure 72, results in collapse of the data for the two
grating widths onto a single master curve, in the same manner as for Lamb waves in films of different thicknesses. The Brillouin data were compared to a calculated Lamb wave for an unsupported film with identical elasticity to the PR film. Although the dispersion of the sub-\( R \) mode was qualitatively similar to the dispersion for the Lamb mode in an unsupported film with thickness \( w \), the data indicate slightly higher velocities. Higher velocity translates to a stiffening of the film, or a higher shear modulus. Geometrically, however, the grating structures are dissimilar to unsupported films in that they are constrained at their base by the SiO\(_x\) substrate that has sound velocities more than two times higher than the polymer.

![Figure 73 Velocity dispersion plot of the sub-Rayleigh mode, scaled to \( Q_||w \), including data from IBM photoresist gratings with 126 nm (hollow stars) and 88 nm (solid stars) widths. The solid line is the calculated dispersion curve for an unsupported film with the same film velocities as in Figure 72, \( V_L = 2.4 \) km/s and \( V_T = 1.3 \) km/s. The closed circles connected by lines are results from finite element calculations for a flexural mode of a grating ridge.](image)

To evaluate the effect of substrate confinement on the sub-\( R \) modes and the apparent stiffening compared to an unsupported film, finite-element (FE) analyses were
performed for the resonant modes of a polymeric nanoline having a cross section of 88 nm × 320 nm with the base fixed. Dr. Paul R. Heyliger at Colorado State University performed the FE simulations and Dr. Ward Johnson at NIST, Boulder correlated the FE calculations to wavevector and frequency values of the flexural modes. The FE simulations employed a three-dimensional representation of the nanoline with a mesh of 2 × 8 × 64 isoparametric brick elements and full integration on all terms. The polymer material was assumed to be elastically isotropic with identical velocities to those found for the supported PR film and used to calculate the Lamb mode for an unsupported film ($V_L = 2.4$ km/s, $V_T = 1.3$ km/s, and $\rho = 1.05$ g/cm$^3$). The frequencies and eigenvectors associated with each mode shape were found using the QR algorithm, which is a standard eigensolver.$^{184}$

A displacement pattern for one of the lowest-order flexural modes determined from the FE calculations is shown in Figure 74a. The displacements of these resonant “Lamb-like” modes are primarily perpendicular to the line directions, consistent with the depolarized Brillouin spectra in Figure 70d and Figure 70e. The corresponding phase velocities of the calculated flexural modes are included in Figure 73 as small, connected circles, and they agree well with the experimental data. Indeed, the simulated velocities for polymeric nanolines with a constraint at a SiO$_x$ substrate are slightly higher than for a completely unsupported film. Recall the polymer parameters ($V_L$, $V_T$, and $\rho$) were identical to that of an unsupported film. Thus the effective velocity increase is solely due to the fixed boundary constraint of the lines.
Figure 74  Visualization of the FE calculations for the (a) sub-Rayleigh mode at $Q_{\parallel} = 17.34 \, \mu m^{-1}$ and $\nu = 2.31$ GHz as a flexural Lamb wave of the grating with width $w$ and (b) Rayleigh mode at $Q_{\parallel} = 11.04 \, \mu m^{-1}$ and $\nu = 2.40$ GHz. The amplitudes of displacements are exaggerated for visual clarity.

The FE analysis reveals the microscopic nature of the new modes observed in these linear nanostructures. Moreover, it suggests that the modulus for shear displacements perpendicular to the scattering plane remains unchanged within the accuracy of our measurements ($\pm 5\%$) down to structure widths of 88 nm. These results are consistent with experiments on free-standing polystyrene films and simulations of nanostructures, which do not predict significant changes in moduli or anisotropic moduli at these length scales.

Brillouin light scattering, as a technique to characterize mechanical properties, was successfully extended from one-dimensionally confined thin films to two-dimensionally confined polymeric nanolines. Brillouin was used to identify acoustic modes localized within and propagating along the nanolines. Further analysis of vibrations localized to the polymeric lines measured in gratings perpendicular to $Q_{\parallel}$ may
also provide insight to and confirmation of shear and longitudinal elasticities. Phonons propagating along the lines were similar to those in supported films, but the sub-Rayleigh mode was unique to the nanolines. Identification of Lamb waves in the grating ridges, and verification using FE calculations, provides an effective mechanism to measure shear modulus in the width direction. If modulus decreases in structures below ~40 nm, as simulations predict, Brillouin will be an excellent technique to quantify the anisotropy of elastic moduli resulting from such nanometric dimensions.

4.3 Poly(methyl methacrylate) (PMMA) Spheres

The Brillouin vibrational spectra of PMMA spheres for two scattering angles are plotted in Figure 75 and are representative of all those measured in the range $14 < Q_{||} < 24 \, \mu m^{-1}$. The Brillouin frequencies from the colloids are $Q_{||}$ independent, indicating localized, non-propagating modes. No propagating ($Q_{||}$ dependent) modes were observed, indicating little or no mechanical coupling between spheres in these colloidal crystals.
Hydration strongly affected the higher frequency Brillouin modes of the PMMA spheres. The effects of de-hydration and re-hydration can be seen in Figure 76. After drying for one day, a strongly polarized mode appeared (green line) near the bulk longitudinal Brillouin frequency for PMMA (black line). Upon re-hydration (100% relative humidity atmosphere), the high frequency spectrum returned to that of the originally prepared sample (blue line).
Figure 76 Brillouin spectra from PMMA spheres measured with p-polarization and p-s polarization after 12 hours of open air exposure and p-polarization after re-hydration.

The spectra of PMMA colloids are consistent with eigenfrequencies typical of non-interacting nanospheres as observed for silica$^{161}$ and polystyrene.$^{162}$ In addition to being $Q_{||}$ independent, the frequencies and relative amplitudes of the PMMA modes were also independent of polarization. This suggests that the spectrum is either completely depolarized or polarization is strongly mixed within the sample. Two vibrations cause depolarized scattering, spheroidal quadrupolar modes (the lowest frequency mode denoted $\nu_2$) and torsional modes. According to theory, the latter do not actively scatter light when $\lambda >> D$. $^{168}$ For calculating transverse sound velocity, the actual distinction between vibrations is not important here, as the lowest frequency torsional mode is degenerate with the lowest frequency spheroidal mode. Most likely, though, the lowest
frequency mode is due to a spheroidal, quadrupolar inner resonance with shear oscillations,\textsuperscript{168} with frequency related to transverse sound velocity by\textsuperscript{169}

\[
V_T \equiv \frac{\nu D}{0.85}
\]

(4.2)

where D is the particle diameter, in this case \(D = 300\) nm. Using this lowest frequency Brillouin mode in Figure 75, \(\nu = 3.91\) GHz, the transverse sound velocity of the PMMA spheres was calculated using equation 4.2 as \(V_T = 1.38 \pm 0.05\) km/s. This experimental value from the spheres is in good agreement with bulk PMMA \(V_T = 1.41\) km/s.\textsuperscript{185}
CHAPTER V

PHONON PROPAGATION IN SILICON OXIDE NANOSTRUCTURES

5.1 Silicon Oxide Film and Gratings

Photolithography has been used for creating patterns for the semiconductor industry for decades. Photoresist polymers used during this process were studied in Chapter IV to evaluate mechanical properties in polymeric structures that exhibit failure below ~100 nm widths. Silicon oxide molds with similar dimensions as the polymeric lines are also used in semiconductor fabrication. Silicon oxide patterns and polymeric lines both rest on a silicon oxide substrate, with similar features sizes, as sketched in Figure 77.

![Figure 77](image)

Figure 77  Cross-sectional schematic of photoresist (PR) lines on SiO$_x$ (left) (50 nm BARC layer omitted) and SiO$_x$ (OX) lines on SiO$_x$ (right). The photoresist is depicted as white and SiOx as gray.
From a phononics standpoint, the photoresist (PR) and silicon oxide (OX) lines rest on substrates of different (PR on SiO$_x$) and similar (SiO$_x$ on SiO$_x$) elasticities. In the photoresist samples, the SiO$_x$ substrate acts as a hard boundary constraint at the base of the lines. In the SiO$_x$ gratings, the SiO$_x$ underlayer does not act as a boundary, but rather a continuous medium for acoustic waves in the lines. Thus, phonons in the photoresist will be reflected from the hard substrate and remain confined within the lines, while phonons in the SiO$_x$ lines do not remain confined, but instead propagate into the SiO$_x$ layer below the base of the lines. The effective height of the SiO$_x$ lines for the sake of calculating velocities of shear vertical waves is the height of the lines plus the film thickness, a total of about 1 µm.

In fact, the SiO$_x$ on SiO$_x$ structures are analogous to polymer lines on a polymer residual layer that are created during nanoimprint lithography, an emerging technology for semiconductor fabrication. Nanoimprint lithography might be able to produce polymeric lines with critical dimensions below 40-50 nm, the length scale at which deviations from bulk behavior have been observed for polymer thin films.$^{8,15}$ However, mass production of such small structures has not yet been realized. As a replacement for polymer lines on a polymer residual layer, Brillouin scattering from the OX gratings can be used to understand the behavior of acoustic waves in gratings resting on substrates of similar elasticity.

Brillouin intensities from silicon oxide (SiO$_x$) films, although ~3 times thicker (~1 µm), were much lower than from the photoresist (PR) films. For example, compare the Rayleigh mode intensity from PR films of ~10 counts/sec to ~2 counts/sec in the SiO$_x$ film spectra in Figure 78 for a ±20 GHz free spectral range (FSR). This fact was
indicative of lower displacement amplitudes contributing to scattering from the ripple mechanism. To increase Brillouin signal, a FSR of ±50 GHz or ±72 GHz was used, but with the same pinhole settings as prescribed for ±20 GHz (300 µm front pinhole, 450 µm rear pinhole) to minimize the width of the elastic line. The differences in intensities for each FSR can be seen in Figure 78.

![Figure 78](image.png)

**Figure 78** Brillouin spectra from SiO\textsubscript{x} film measured at $Q_{||} = 14 \, \mu m^{-1}$ for 3 different free spectral ranges.

Also, incident power was increased to nearly the maximum allowable by the setup. Previous Brillouin studies of SiO\textsubscript{x} and other inorganic films discussed in Chapters II and III used incident powers of at least 70-150 mW to achieve reasonable signal statistics\textsuperscript{146}. Experimental setups in this study limited the incident power of horizontally polarized light ($p$-polarization) to 90-100 mW with the small mirror and ~30 mW with the semi-transparent mirror as the backscattering mirrors. Spectra obtained with the small mirror were used to determine the nature of modes (incident and scattered light
polarization dependence) and comparing film and gratings spectra, while those collected using the semi-transparent mirror were used for comparison to calculated dispersion relationships.

Figure 79 shows Brillouin spectra from the SiO$_x$ film measured at various $Q_{||}$ with the small mirror as the backscattering mirror. The propagating nature of the surface waves can be seen by their $Q_{||}$ dependence. Note how the frequencies of the surface waves become closer together at low $Q_{||}$, complicating peak fitting and mode designation.

![Figure 79](image)

Figure 79 Brillouin spectra from the SiO$_x$ film measured at $Q_{||} = 10.3$, $17.3$, and $22.5$ µm$^{-1}$ ($\theta = 25$, $45$, and $67^\circ$).

Note the difference between the film and gratings spectra for a given $Q_{||}$ (14 µm$^{-1}$, Figure 80). As in the polymer gratings, a mode below the Rayleigh mode appears, denoted here also as the sub-Rayleigh (sub-R) mode. For comparison to Figure 80, the corresponding Brillouin spectra are shown in Figure 81 when the semi-transparent mirror
was used as the backscattering mirror (see Section 3.2 for details). The incident power, and therefore signal intensity, was much lower when using the semi-transparent mirror,

![Figure 80](image1)

Figure 80  Brillouin spectra of the SiO$_x$ film and 148 nm and 112 nm gratings measured at $Q_{\parallel} = 14 \ \mu$m$^{-1}$ ($\theta = 35^\circ$) using the small mirror as the backscattering mirror.

![Figure 81](image2)

Figure 81  Brillouin spectra of the SiO$_x$ film and 148 nm and 112 nm gratings measured at $Q_{\parallel} = 14 \ \mu$m$^{-1}$ using the semi-transparent mirror as the backscattering mirror.
and signal intensity was even lower for $p$-$s$ polarization. However, absolute frequencies were more accurate than measurements with the small mirror, so spectra similar to those in Figure 81 were used for calculating velocities for comparison with calculated values from theory. The low frequency Brillouin modes from the SiO$_x$ film and 148 nm and 112 nm gratings are plotted in the dispersion plot in Figure 82. Notice the sub-Rayleigh modes are unique to the grating structures and are grating width dependent.

![Figure 82](image)

Figure 82  Frequency dispersion plot of SiO$_x$ film and grating sub-Rayleigh (Sub-R), Rayleigh (R), and Sezawa/Shear horizontal (S1/SH2) Brillouin modes.

The characteristic features of the sub-Rayleigh mode in the SiO$_x$ gratings are the same as in the polymer gratings: i) appears in gratings but not in the film, ii) velocity decreases with decreasing $Q_{\parallel}$, iii) rescales to width of the gratings for a master curve, and iv) appears in depolarized ($p$-$s$ polarization) scattering. The first three characteristics can be seen in Figure 83, where the sub-Rayleigh velocities in the gratings are scaled to width.
and compared to the zero order antisymmetric Lamb wave of an unsupported (free-standing) SiO$_x$ film (recall Figure 32 in Chapter II for free-standing waves), as calculated by equation 2.35 (Mathematica Appendix C).

In calculations of dispersion curves for surface waves in SiO$_x$ layers, the parameters used for the SiO$_x$ layer were $V_{L,\text{SiO}_x} = 5.95$ km/s, $V_{T,\text{SiO}_x} = 3.74$ km/s, and $\rho_{\text{SiO}_x} = 2.2$ g/cm$^3$, and for the Si substrate $V_{L,\text{Si}} = 8.94$ km/s, $V_{T,\text{Si}} = 5.34$ km/s, and $\rho_{\text{Si}} = 2.33$ g/cm$^3$. In the case of the lowest order Lamb wave in Figure 83, the substrate velocities were set equal to zero in the matrix equation 2.29. The Rayleigh velocity of SiO$_x$, represented by a dashed line in Figure 83 and Figure 85, was calculated from equation 2.34 as $V_R \sim 3.39$ km/s.

![Figure 83 Velocity dispersion of the sub-Rayleigh mode in 112 nm (triangles) and 148 nm (circles) gratings. The calculated zero order antisymmetric Lamb mode for an unsupported SiO$_x$ film is shown for comparison. The Rayleigh velocity of SiO$_x$ is shown as the dashed line.](image)

The sub-Rayleigh velocities of the SiO$_x$ gratings are slightly higher than those of an unsupported SiO$_x$ film but qualitatively follow the same dispersion behavior. This
small increase of less than 5% can be partially explained by the boundary constraint at the base of the gratings. The appearance of the sub-Rayleigh mode in depolarized ($p-s$ polarization) scattering (Figure 84) is further evidence that this sub-Rayleigh mode observed in SiO$_x$ is of the same nature as that in the polymeric lines. The sub-Rayleigh mode can be thought of as a pseudo-Lamb wave of the unsupported sidewalls of the structure. In other words, compared to the shear vertical displacements of the Rayleigh and Sezawa modes, the sub-Rayleigh mode is a type of shear horizontal mode. Surprisingly, the sub-Rayleigh is not the only Brillouin mode that appears under $p-s$ polarization.

Figure 84  Brillouin spectra from the SiO$_x$ film and 148 nm gratings under $p-ps$ and $p-s$ polarization conditions ($Q_{||} = 14$ µm$^{-1}$).

As seen in Figure 84, spectra collected using $p-s$ polarization revealed a mode in the film and the gratings, at a frequency higher than either the sub-Rayleigh or Rayleigh
modes. In fact, the frequency corresponded to the high frequency shoulder of the Rayleigh peak observed in $p$-$ps$ polarization. Rayleigh-type, or Sezawa modes, have shear vertical (transverse in the sagittal plane) displacements and should not be visible under $p$-$s$ polarization. The polarization dependence of this mode suggests it is associated with a shear horizontal (SH) wave in the SiO$_x$ layer. Recall that waves with velocity below the substrate transverse velocity (in this case $V_{T,\text{Si}} = 5.34 \text{ km/s}$) belong to the discrete spectrum. So, the SH waves seen in the SiO$_x$ layers belong to the discrete spectrum and are known as Love waves.

Figure 85 shows the velocities of Brillouin modes from the SiO$_x$ film and gratings spectra, measured using the semi-transparent mirror, with the corresponding theoretical dispersion curves as calculated by the matrix equation 2.29 for shear vertical (Rayleigh-type) and shear horizontal (Love) waves. The velocity dispersion relationships for Love waves were calculated using equation 2.36 in the Mathematica program in Appendix D. The velocities of the second order Love (SH) mode coincide with the velocities of the first Sezawa (SV) mode.

Regarding spectra of SiO$_x$ gratings (110 nm particularly) measured using $p$-$s$ polarization with the semi-transparent mirror, signal strength was too weak to discern a SH wave other than the sub-Rayleigh mode. Therefore, the frequencies of SH modes were inferred from overlapping peaks in $p$-$ps$ measurements.

For most spectra, the broad, low frequency multi-mode was fit with two Lorentzian lineshapes that resulted in two modes corresponding to the Rayleigh and first order Sezawa mode. Experimental uncertainties were estimated from one standard
deviation of the average of positive and negative Brillouin frequency shifts, on average ~3% for $Q_{||} = 10$ and 14 $\mu$m$^{-1}$ and ~2% for $Q_{||} = 17$ and 20 $\mu$m$^{-1}$.

Figure 85  Velocity dispersions for Brillouin data from the SiO$_x$ film (squares) and 112 nm (triangles) and 148 nm (circles) gratings. The calculated relationships for shear vertical Lamb, Rayleigh, and Sezawa modes (thick lines) and shear horizontal Love waves (thin lines) are also shown. Dashed lines represent the transverse and Rayleigh velocities of SiO$_x$.

As mentioned above and seen in Figure 79 and Figure 81, the Brillouin peaks from the SiO$_x$ surface waves at $Q_{||} = 10$ and 14 $\mu$m$^{-1}$ strongly overlap, making it difficult to distinguish individual modes. Differentiating these modes using p-s polarization was difficult because statistics were so low. In the absence of these measurements, the frequencies of Sezawa and Love modes were inferred from overlapping peaks in $p$-$ps$ measurements. Consequently, as seen in Figure 85, the uncertainty in velocities increased slightly at lower $Q_{||}$, and it is possible that additional modes could be identified.
with better signal statistics (requiring higher incident power, longer collection times, lower FSR) or \( p-p \) polarization. At least in the film and 148 nm gratings, the first order Love/SH1 mode was distinguishable at \( Q_{\parallel}d = 10 \ \mu \text{m}^{-1} \) (Figure 85).

As an example of Brillouin peak overlap, the second lowest frequency/velocity peak for the 112 nm gratings at \( Q_{\parallel} = 10 \ \mu \text{m}^{-1} \) is estimated just between SH1 and S1/SH2 (Figure 85). This mode was fit as one of two Lorentzian peak shapes to the spectrum in Figure 86, and can best be described as a ‘Sezawa-like’ mode (S1/SH2). It was not possible with this data set to fit three Lorentzians, but the broad feature might contain Brillouin scattering from at least three acoustic vibrations in the SiO\(_x\).

![112 nm SiO\(_x\) grating at \( Q_{\parallel} = 10 \ \mu \text{m}^{-1} \)](image)

Figure 86  Brillouin spectrum of 112 nm SiO\(_x\) gratings at \( Q_{\parallel} = 10 \ \mu \text{m}^{-1} \). The Rayleigh (R) and ‘Sezawa-like’ (S1/SH2) mode frequencies are shown with arrows.

Unlike low \( Q_{\parallel} \) values (10 and 14 \( \mu \text{m}^{-1} \)), signal strength was high enough at high \( Q_{\parallel} \) values (17 and 20 \( \mu \text{m}^{-1} \)) using the semi-transparent mirror and \( p-s \) polarization to
distinguish SH modes other than the sub-Rayleigh mode. Figure 87 shows $p$-$s$ polarization spectra of the 112 nm and 148 nm silicon oxide gratings at $Q_{\parallel} \sim 17 \, \mu m^{-1}$ ($45^\circ$), and can be compared to the Brillouin modes observed for silicon oxynitride films in Figure 30 (After Ref. 146). Notice, however, the broad mode with SH character, with significant broadening on the low frequency side, near the frequency of the Rayleigh mode. This SH character could result from either the SH1 and SH2 modes or a Rayleigh mode in the oxide gratings with polarization mixing. That is, the Rayleigh mode in the gratings might have some shear horizontal component.

![Brillouin spectra](image)

**Figure 87** Brillouin spectra for (a) 112 nm and (b) 148 nm wide silicon oxide grating lines on silicon, oriented parallel to $Q_{\parallel} = 17 \, \mu m^{-1}$ ($\theta = 45^\circ$) with incident polarization in the scattering plane ($p$-polarization). The polarization of the scattered light was measured without a polarization analyzer ($p$-$ps$) and with an analyzer selecting $s$-polarization ($p$-$s$). The semi-transparent mirror was used as the backscattering mirror.

A low-frequency broadening of the SH mode(s) is also observed, although to a lesser extent, in $p$-$s$ polarization measurements using the small mirror as the backscattering
mirror. Depolarized \((p-s)\) scattering spectra of the SiO\(_x\) film does not show low-frequency broadening of the SH mode(s). Figure 88 shows Brillouin spectra of the 112 nm SiO\(_x\) gratings measured using \(p-ps\) and \(p-s\) polarizations with the small mirror, for comparison to Figure 87a from measurements with the semi-transparent mirror.

![Figure 88](image)

Figure 88  Brillouin spectra from 112 nm SiO\(_x\) gratings at \(Q_{||} = 17 \ \mu m^{-1}\) measured with the small mirror as the backscattering mirror.

It is unclear why \(p-s\) polarization with the semi-transparent mirror showed stronger polarization mixing than the small mirror (intensity of Rayleigh mode relative to SH mode), but it is likely related to scattering statistics and low intensities for the SH modes. Polarization tests indicated that the semi-transparent mirror did not cause polarization rotation upon reflection or transmission. Thus, as a real phenomenon, it is worthwhile to consider possible origins of polarization mixing.

As shown in reference 112, surface waves propagating along shallow grooves cannot exist with either pure shear vertical (sagittal) or pure shear horizontal polarization.
Instead, the stress-free boundary conditions create modes with mixed shear vertical and horizontal polarizations in the so-called selvedge region (“region between the minimum and maximum excursions of the surface from planarity”\textsuperscript{112}). In the high aspect ratio grating lines considered in this study, the effect of polarization mixing was likely amplified by the excess free surfaces. Brillouin zone-folding observed in shallow grooves (corrugated surfaces) occurred through a hybridization of the Rayleigh wave and longitudinal resonances.\textsuperscript{112} Thus it is possible that the Rayleigh wave in the grating lines hybridizes with the SH mode in the underlayer. Polarization mixing should not be expected in supported SiO$_x$ films without grooves or gratings. This was supported by the absence of low frequency broadening of the SH mode(s) in depolarized ($p$-$s$ polarization) measurements of films with the small mirror.

Several interesting features were observed for the SiO$_x$ films and gratings. First, SiO$_x$ gratings spectra revealed a sub-Rayleigh mode, or a type of shear horizontal mode, similar to that observed in the polymeric gratings. This sub-Rayleigh mode is apparently associated with an antisymmetric Lamb wave that ripples the surfaces of the sidewalls of the SiO$_x$ structures. Second, both the SiO$_x$ film and gratings spectra contain at least one higher frequency shear horizontal wave. Observation of SH waves is consistent with previous Brillouin studies of oxide films on a semiconductor substrate. Depolarized ($p$-$s$ polarization) scattering helped identify the nature of the SH modes, partially distinguishing Love modes from Sezawa modes that appear at very similar frequencies but are related to different elastic tensors of modulus. Third, a possible low-frequency shoulder of the SH mode(s) in $p$-$s$ scattering from SiO$_x$ gratings suggests that the excess free surfaces of the gratings cause some polarization mixing of the Rayleigh wave.
5.2 Phonon Propagation in Periodic Structures

One goal of studying acoustic wave propagation in the silicon oxide structures was to understand the effect of substrate interactions on modes in the gratings for a system with well-known elastic constants. Such analysis provides useful information for Brillouin spectroscopy of nanoimprinted polymer gratings on a residual polymer layer. In particular, behavior of the newly discovered sub-Rayleigh mode should show substrate dependency, because the bases of the grating lines are dependent on boundary conditions at the substrate.

The sub-Rayleigh velocities in both photoresist lines and SiO\textsubscript{x} lines on SiO\textsubscript{x} substrates qualitatively behaved as a Lamb wave in a free-standing plate with identical elastic constants as the grating line medium. As discussed in Chapter IV, the photoresist sub-Rayleigh velocities were slightly higher than the velocity of the Lamb wave. The increased velocity was explained using a constrained base in finite element (FE) simulations. The hard substrate effectively increased the shear velocity in the width direction of the polymeric lines. The SiO\textsubscript{x} sub-Rayleigh velocities more closely matched the Lamb velocities of a free-standing plate. Apparently the sub-Rayleigh velocity is not as strongly affected by a boundary constraint when the gratings and substrate have matching elasticities. Moreover, agreement of sub-R modes with calculated dispersion is better at higher $Q_{\text{u}}$ where shorter wavelength phonons are probed. This is to be expected because as $\lambda_{\text{ph}}$ becomes less than feature height the phonon velocity should be less affected by substrate constraints and closer to the velocity in a truly free-standing film.
The measured sub-Rayleigh velocities and corresponding Lamb mode calculations are plotted in Figure 89 for comparison.

![Figure 89](image)

**Figure 89** Velocity dispersions of the sub-Rayleigh modes in the (a) polymeric and (b) SiO\textsubscript{x} lines. The Brillouin measured data points are compared to the calculated dispersion curves for the zero order antisymmetric (A\textsubscript{o}) mode for a free-standing plate of (a) photoresist and (b) silicon oxide.

Although substrate effects can be explained qualitatively, more detailed simulations will likely be necessary to calculate more specific effects. For example, determining size-dependent elastic moduli of nanoimprinted structures will depend on how well one understands effects of substrate elasticity and thickness. Still, the SiO\textsubscript{x} measurements provide a guide for the degree of substrate effects to expect in nanoimprinted polymer lines with a polymer residual layer.

Another interesting difference between the polymeric and oxide films was the polarization dependence of some modes. For example, whereas the Brillouin spectra for \textit{p-s} polarization for polymer films was featureless, the Brillouin spectra under depolarized scattering conditions for the SiO\textsubscript{x} films revealed a single peak. The frequencies of this single mode agreed with theory for the second order shear horizontal, or Love wave, calculated from equation 2.36 using the sound velocities of silica. The agreement
between Love wave calculations and shear horizontal velocities means that SH modes at frequencies above the sub-Rayleigh mode provide a means to measure a shear horizontal modulus of the SiO\textsubscript{x} underlayer.

Recall from Chapter II that previous studies of oxide and nitride films on semiconductor substrates yielded shear horizontal waves that appeared under \textit{p-s} polarization conditions\textsuperscript{146,153}. Scattering from shear horizontal modes occurs purely from the elasto-optic mechanism, that is the scattering from the periodic modulation of the dielectric tensor due to acoustic phonons. Therefore the intensity of Brillouin modes from SH waves is related to the strength of volume elasto-optic coupling and the volume of the scattering medium. Previous cases in which SH waves were observed studied films at least 1 \textmu m thick\textsuperscript{146} and have shown thickness dependent intensity. These studies also note that SH resonances can only be observed for strong elasto-optic media\textsuperscript{146}. As determined by Sun \textit{et al.}, the elasto-optic coefficients of polystyrene films, which for comparison will be used in place of the photoresist material, were \(k_{11}(\text{PS}) = -1.4 \pm 0.4\) and \(k_{12}(\text{PS}) = -1.6 \pm 0.4\)\textsuperscript{69}. These values are about three times greater than those for SiO\textsubscript{x}, \(k_{11}(\text{SiO}_x) = -0.55\) and \(k_{44}(\text{SiO}_x) = 0.345\)\textsuperscript{151}, indicating that elasto-optic scattering might actually be greater for polymeric films. However, SiO\textsubscript{x} films were \textasciitilde1 \textmu m thick, compared to \textasciitilde370 nm thickness for polymeric films, which most likely explains why the SH modes appeared only for SiO\textsubscript{x} films.
5.2.1 Brillouin Modes of Silicon Oxide Gratings Oriented Perpendicular to $Q_{||}$

The main observations and conclusions in the above studies resulted from Brillouin measurements of grating lines oriented parallel to the scattering wavevector $Q_{||}$. Previous studies of wave propagation in periodic media concentrated on propagation across periodic Si features, in which shallow gratings (corrugations) introduced zone boundaries, but neither zone-folding nor phononic bandgaps were observed in the experiments described here. This section summarizes the qualitative findings from measurements of SiO$_x$ grating lines oriented perpendicular to $Q_{||}$. Gratings measured parallel to $Q_{||}$ were oriented horizontally, so gratings perpendicular to $Q_{||}$ were oriented vertically.

Slightly different characteristics were observed for each of the two grating widths, 148 nm and 112 nm, when oriented vertically as compared to horizontally. In general, the frequencies of the modes were similar for both orientations, but the ratios of intensities were slightly different. Vertically oriented 148 nm gratings (measured at $Q_{||} \approx 10, 17$, and $22 \, \mu m^{-1}$) did not result in any sub-Rayleigh mode or $Q_{||}$ independent mode, but showed a weak Rayleigh mode and a prominent SH mode. Figure 90 illustrates the difference between Brillouin spectra from horizontally and vertically oriented 148 nm SiO$_x$ gratings for $p$-polarization. Most noticeably for the vertical 148 nm gratings, the sub-Rayleigh mode was completely suppressed and the Rayleigh mode was strongly suppressed compared to the horizontal gratings. The complex structure near 15 GHz in Figure 90 is likely a hybridization of Sezawa and longitudinal waves (S-LW) of the SiO$_x$ underlayer,
as seen in Ref. 149. For 148 nm gratings, the principal (low-frequency) surface waves of the grating lines were not found to propagate across the SiO\textsubscript{x} lines.

Figure 90  Brillouin spectra of 148 nm SiO\textsubscript{x} gratings measured at $Q_{\parallel} = 17 \, \mu m^{-1}$ with gratings oriented parallel (thick line) and perpendicular (thin line) to $Q_{\parallel}$.

Figure 91 illustrates the Brillouin spectra under $p$-polarized conditions when 112 nm gratings were oriented vertically (perpendicular to $Q_{\parallel}$). Like the 148 nm gratings, the Rayleigh mode was suppressed compared to the horizontal gratings. Unlike the 148 nm gratings, limited measurements of the 112 nm vertical gratings reveal a possible $Q_{\parallel}$ independent mode appearing at $6.37 \pm 0.2 \, GHz$ at $Q_{\parallel} = 14 \, \mu m^{-1}$ and $6.24 \pm 0.2 \, GHz$ at $Q_{\parallel} = 17.3 \, \mu m^{-1}$. An average frequency $\sim 6.3 \, GHz$ lies between the sub-Rayleigh modes at each $Q_{\parallel}$ (measured with gratings parallel to $Q_{\parallel}$). This is the only apparently $Q_{\parallel}$ independent mode observed for OX gratings oriented perpendicular to $Q_{\parallel}$, in contrast to the three observed for 88 nm PR gratings. A reasonable confinement dimension results from a first approximation where one half wavelength exists within the confining walls,
\[ D_c = \frac{V_T}{2\nu} \]. Using an average frequency of 6.3 ± 0.4 GHz and \( V_{T,\text{SiO}_x} = 3.74 \text{ km/s} \), \( D_c = 300 \text{ nm} \pm 20 \text{ nm} \), which indicates this may be a transverse mode associated with the height of the OX grating lines, ~320 nm. However, the spectra in Figure 91 provide the only evidence of localized modes in SiO\(_x\) gratings. It is unclear why such modes were not observed in the 148 nm gratings. This approximation does not apply universally to vertically oriented SiO\(_x\) gratings, but instead serves as a preliminary exercise for future studies of gratings with similar elasticity to the underlying substrate.

![Figure 91](image)

Figure 91  Brillouin spectra of 112 nm SiO\(_x\) gratings measured at \( Q_{||} = 14 \mu\text{m}^{-1} \) and \( Q_{||} = 17.3 \mu\text{m}^{-1} \) with gratings oriented perpendicular to \( Q_{||} \).

Vertical gratings were also measured using \( p\)-\( s \) polarization. For 112 nm vertical SiO\(_x\) gratings at \( Q_{||} = 14, 17, \) and \( 20 \mu\text{m}^{-1} \), the SH mode was the only visible mode in \( p\)-\( s \) polarization measurements (shown for \( Q_{||} = 17 \mu\text{m}^{-1} \) in Figure 92). That is, the localized mode disappears in depolarized measurements, indicating a shear vibration in the height direction of the grating line sidewalls. The appearance of the SH mode in vertical SiO\(_x\)
gratings is consistent with the presence of the SH mode in the SiO\textsubscript{x} film, further suggesting the SH mode propagates within the SiO\textsubscript{x} layer beneath the gratings. From the shape of the SH mode, it is difficult to conclude whether the Rayleigh mode shows any SH component when grating orientation is perpendicular to $Q_{||}$.

Figure 92  Brillouin spectra of 112 nm SiO\textsubscript{x} gratings measured at $Q_{||} = 17$ µm\textsuperscript{-1} with gratings oriented parallel (thick and thin lines) and perpendicular (dashed line) to $Q_{||}$.

Brillouin spectra from SiO\textsubscript{x} grating lines oriented perpendicular to $Q_{||}$ generally showed the same modes as SiO\textsubscript{x} lines parallel to $Q_{||}$, except the disappearance of the sub-Rayleigh mode, partial suppression of the Rayleigh mode, and appearance of the possible $Q_{||}$ independent (localized) mode. The possible $Q_{||}$ independent mode in spectra of 112 nm vertical OX lines had frequencies in the range of the sub-Rayleigh mode, but if localized, it may be associated with a shearing of the grating lines in the height direction. More positive identification of this mode will require spectra from more scattering angles; note its appearance in $p$-$ps$ polarization (Figure 91) but not in $p$-$s$ polarization.
(Figure 92). The spectra of 148 nm vertical OX lines did not reveal a $Q_\parallel$ independent mode under any polarization conditions. Partial suppression of the Rayleigh mode when gratings were perpendicular to $Q_\parallel$ suggests it mainly propagates along the SiO$_x$ grating lines, and only weakly across them. This is in contrast to PR gratings in which the Rayleigh mode did not propagate across grating lines.

5.2.2 Dependence on Incident Polarization

All previously discussed spectra were collected using $p$-polarized incident light. It was found that using $s$-polarization conditions for a SiO$_x$ film, a strong mode appeared at frequencies above the same strong modes observed using $p$-polarization (near 11 GHz in Figure 93).

![Brillouin Spectra](image)

Figure 93 Brillouin spectra from a silicon oxide film on silicon using $p$- (thick black) or $s$- (thin gray) polarizations at $Q_\parallel = 10 \mu$m$^{-1}$ ($\theta = 25^\circ$).
A combination of the above two variables, grating orientation and incident polarization, was used for 112 nm SiO$_x$ gratings at $Q_{\|} = 14 \mu m^{-1}$. As discussed above, a possibly $Q_{\|}$ independent mode appears in the range of the sub-Rayleigh frequency in vertical gratings compared to horizontal gratings. More noticeably, the s-polarization measurements reveal the same strong mode near the Rayleigh frequency of Si as observed for the SiO$_x$ film in Figure 93.

![112 nm OX Gratings; $Q_{\|} = 14 \mu m^{-1}$](image)

Figure 94  Brillouin spectra from 112 nm OX gratings oriented parallel (top) and perpendicular (bottom) to $Q_{\|}$ measured at $Q_{\|} = 14 \mu m^{-1}$ using $p$-polarization (thick lines) and $s$-polarization (thin lines).

The nature of the vibrations associated with this wave is unclear. This strong mode consistently appears at frequencies slightly higher than the Rayleigh frequency of a clean Si(100) wafer. It is possible that the frequency is shifted slightly because the cut of Si is different from the (100) direction, or the wafer might be doped such that the modulus is greater than undoped Si(100). In any case, the penetration depth of s-
polarization through the Si substrate should be higher than for p-polarization, which would lead to higher scattering intensity from the Si substrate.

5.3 Summary of Results from Silicon Oxide Gratings

Overall, the observations from SiO$_x$ grating lines oriented perpendicular to $Q_{||}$ indicated that apparently the same modes propagate along and across the OX lines, except the sub-Rayleigh mode. Interestingly, vertically oriented 112 nm gratings revealed a possible $Q_{||}$ independent mode but 148 nm gratings did not reveal any such mode. The strong mode seen from s-polarization is interesting, but its significance is yet unclear, although it is likely related to the Si substrate.

Brillouin spectra from both polymer-on-SiO$_x$ and SiO$_x$-on-silicon films and gratings contained shear vertical (SV) waves, such as Rayleigh, Sezawa, and Lamb modes. SV waves have been well-documented for damping films, for which the transverse velocity in the film is less than in the substrate, and SV modes were also found to propagate along the grating lines. Additionally, a low frequency shear horizontal wave (sub-Rayleigh), not present in the films, propagated along both SiO$_x$ and polymeric gratings. The dispersion behavior of the sub-Rayleigh mode was similar to a zero order antisymmetric Lamb wave of a free-standing plate, although slightly stiffened by the constraint at the substrate, and to a greater extent in the case where the substrate was much stiffer than the propagating medium, polymer lines on SiO$_x$. In SiO$_x$ film and gratings, in addition to a sub-Rayleigh mode, a higher frequency shear horizontal wave was observed, classified as a discrete Love mode. Polarization dependence was used to
identify shear horizontal modes capable of providing information about possible anisotropic elastic constants in nanostructures.

The features of the Brillouin spectra from SiO$_x$ films and gratings, and their comparisons to photoresist lines, may help interpret future phononics studies of polymeric lines created by nanoimprint lithography. The residual layer of the SiO$_x$ (OX) lines apparently allowed similar phonon propagation along and across the OX lines whereas the hard substrate under the photoresist (PR) lines resulted in very different spectra for PR lines parallel and perpendicular to $Q_{||}$. The interpretation of localized modes observed with grating lines oriented perpendicular to $Q_{||}$ remains a challenge.

The realization of Brillouin spectroscopy for measuring mechanical properties of nanostructures will depend on accurate identification of phonon propagation from Brillouin spectra using various polarization schemes and sample orientations relative to the scattering wave vector $Q_{||}$. As demonstrated in this and the previous chapter, the phononic spectra of waves propagating along the polymeric and SiO$_x$ grating lines allowed determination of modulus and its anisotropy. The SiO$_x$ lines rest on a residual layer of identical elasticity, implying the observations and conclusions of these studies will provide guidance for the phononic spectrum and its relationship to elastic constants for nanoimprinted structures that typically also rest on a residual layer.
CHAPTER VI

VIBRATIONS AND MECHANICS OF BIOLOGICAL NANOSTRUCTURES

One might expect Wiseana iridescent virus (WIV), as a biological sphere-like particle, to have vibrational eigenfrequencies similar to the polymeric spheres discussed in Section 4.3, or those predicted by Talati and Jha. On the other hand, WIV is a more complex particle, with a core-shell structure and surface fibrils. As seen by the results discussed in the following sections, interpretation of Brillouin spectra from WIV was not as straightforward as it was for PMMA spheres.

6.1 Wiseana Iridescent Virus Assemblies

Initial measurements were performed on WIV samples cast onto Al mirrors. Aluminum mirrors were initially chosen to avoid spectral overlap of the substrate modes with the Brillouin modes from viruses. Unfortunately, the Al mirrors were not ideal substrates because surface modes of the Al still interfered with the Brillouin modes from the WIV. However, these initial studies provide qualitative insight for the effect of relative humidity (RH) on the WIV modes, as measured in a custom-built humidity chamber.
Relative humidity did not strongly influence the Brillouin spectra of WIV multilayers on Al. Representative spectra for WIV multi-layers, at 0% and 100% RH, are shown in Figure 95. By contrast, relative humidity did affect Brillouin spectra of WIV monolayers. At high $Q_{||}$, the Brillouin peaks above 10 GHz were completely suppressed when relative humidity was increased from 0% to 100%, but RH did not affect the WIV mode near 6 GHz or the Al mode near 8 GHz (Figure 96).

At lower $Q_{||}$, increased humidity suppressed the mode from WIV (e.g. WIV mode near 5 GHz in Figure 97), indicating dampening of longer wavelength vibrational modes by the increased moisture content in the environment surrounding WIV. The fact that phonons with $\lambda_{ph} > \sim 330$ nm ($Q_{||} < 18.7$ $\mu$m$^{-1}$) are more strongly affected by relative...
humidity than shorter wavelength phonons indicates that RH affects long-range interparticle interactions. Juhl et al. found that increased water content increased the

**Monolayer WIV on Al, θ = 50°**

![Graph](image)

Figure 96  Brillouin spectra from a monolayer of WIV on Al at $Q_\parallel = 18.7 \, \mu m^{-1}$ at 0% RH (thick line) and 100% RH (thin line).

**Monolayer WIV on Al, θ = 35°**

![Graph](image)

Figure 97  Brillouin spectra from a monolayer of WIV on Al mirror at $Q_\parallel = 14 \, \mu m^{-1}$ ($\theta = 35°$), 0% and 100% RH. The Brillouin peak near 6.5 GHz is from the Al substrate.
inter-virion spacing and suggested this phenomenon was due to swelling of virions.\textsuperscript{96} It is likely the adsorbed water from the atmosphere to the surfaces of the virions damps the amplitude and lifetime of vibrations in and between WIV virions. A representative Brillouin spectra is shown in Figure 97 in which the Al mode appears at 6.5 GHz and the surrounding WIV modes become less distinct at high RH.

Using a silicon substrate instead of aluminum mirror decreased the scattering intensity from the virus layers. More importantly, though, the spectral interference from the substrate was eliminated. Notice in Figure 98 the mixture of the strong Al mode near 10 GHz with a strong WIV mode, as seen from the spectra of WIV on Si. By contrast, the Rayleigh surface wave of Si at $Q_\parallel = 20 \, \mu m^{-1}$ is ~15 GHz, which is not observed in the spectra from the multi-layers of WIV on Si. The spectra in Figure 98 show that when WIV is placed on Si, the WIV mode at ~10 GHz is distinguishable (thin line), and is not convoluted by the Al surface mode (thick line).

![Figure 98](image-url)

**Figure 98** Brillouin spectra of multi-layers of WIV on Al (thick line) and Si (thin line) at $Q_\parallel = 20 \, \mu m^{-1}$ ($\theta = 55^\circ$).
Brillouin spectra of WIV on Si reveal $Q_{||}$ dependent modes, as seen in Figure 99 for three values of $Q_{||}$. This is in sharp contrast to the $Q_{||}$ independent modes seen for multi- and monolayers of PMMA on Al and Si. Recall propagating modes are $Q_{||}$ dependent and localized modes are $Q_{||}$ independent. Whereas vibrations in PMMA spheres were strongly localized within the confines of each single particle, vibrational modes in multi-layered WIV propagate from one virus particle to another. Apparently, there is a strong mechanical coupling between the WIV particles that promotes the propagation of acoustic modes. This coupling may arise from entanglement of the fibrillar structures extending from the capsid shell or from long-range charge interactions.

![Figure 99](image.png)

Figure 99 Brillouin spectra from multi-layered WIV on Si for $Q_{||} = 20, 17, \text{ and } 14 \, \mu m^{-1}$, clearly illustrating the $Q_{||}$ dependence, or propagating nature, of these Brillouin modes.

Full dispersion curves of the multi-layers of WIV modes could not be fit to a simple film on a Si substrate model, which is perhaps indicative of the heterogeneity of
the films. Spacings between viruses, surface roughness, and complex particle structure strongly scatter long wavelength phonons. Short wavelength phonons, however, should propagate more easily. Therefore, probing short wavelength phonons at $Q_{||}d > 2\pi$ yields elasticity information about the layer unaffected by the substrate.

The thickness of the WIV multi-layered assembly is not uniform, but ranges from about 0.8 to 1 $\mu$m, as estimated by profilometry at the film edges and scratches. Thus, measurements at $Q_{||} = 17$ and 20 $\mu$m$^{-1}$ were well above the threshold $Q_{||}d > 2\pi$ for probing short wavelength phonons. At these high $Q_{||}$ values, the Rayleigh velocity of the film-like virus layer was $1.44 \pm 0.10$ km/s, as seen in Figure 100.

![Figure 100](attachment://Figure100.png)

**Figure 100** Velocity dispersion plot of WIV multi-layers on Si with the asymptotic Rayleigh velocity marked for the film-like WIV layer.

To determine $V_T$ from $V_R$ of the propagating modes, a Poisson ratio, $\sigma$, must be assumed. For biological objects, this quantity is usually in the range $\sigma = 0.3-0.4$.$^{101,102}$ For consistent approximations (as described in Section 6.3), Poisson’s ratio was assumed...
to be $\sigma = 0.33$, a value at which $V_L = 2V_T$ and $V_R \approx 0.93V_T$. This yields $V_T = 1.55 \pm 0.10$ km/s and a rough estimate of $V_L \approx 3$ km/s. These sound velocities indicate that the WIV film-like assemblies are mechanically similar or even stiffer than a PS or PMMA film.

6.2 Individual Wiseana Iridescent Viruses

Virus coverage on the Si wafer was reduced to monolayer coverage in an attempt to detect $Q$-independent Brillouin modes from the localized vibrations of individual virus particles. In fact, $Q_{||}$ independent modes with frequency near 9 GHz were observed in a WIV monolayer on Si (Figure 101).

![WIV Monolayer on Si](image)

Figure 101 Brillouin spectra from a WIV monolayer on Si at three $Q_{||}$ values measured with FSR ±72GHz.
The monolayer WIV spectra collected with a lower FSR (±50 GHz) yielded not only the same $Q_{||}$ independent modes, but also $Q_{||}$ dependent modes at frequencies below 9 GHz. The frequency dispersions of both modes are shown in Figure 102.

![Figure 102](image_url)

**Figure 102** Brillouin frequencies from a WIV monolayer on Si from spectra measured using FSR 50 GHz, in which propagating modes were observed at frequencies below the localized mode.

As in multilayered assemblies of WIV, the propagating modes in the WIV monolayer indicate there is also some mechanical coupling between virions. However, measurements of a monolayer ($d \sim 0.14 \mu m$) cannot reach the asymptotic values at $Q_{||}d > 2\pi$ because $Qd_{\text{max}} \sim 3$. This limitation precludes estimates of sound velocities from monolayer “film-like” modes.

Reducing the surface coverage of WIV even further (sub-monolayer) provided the opportunity to observe only localized virion vibrations. Amazingly, a mode unique to the virus sample was detected with an extremely low surface coverage of WIV (<20
virions/µm³) on Si. The Rayleigh mode of silicon is the most prominent in the Brillouin spectra from these samples with sub-monolayer coverage of WIV on a silicon wafer (Figure 103). The large distances between virions eliminate any means for mechanical coupling and thus eliminate $Q_\parallel$ dependent acoustic modes.

![Sub-monolayer WIV on Si](image)

Figure 103. Brillouin spectra from a sub-monolayer of WIV coverage on Si at $Q_\parallel = 20$ and 24 µm⁻¹, with comparison to the Si substrate spectra at $Q_\parallel = 20$ µm⁻¹.

The single Brillouin mode observed from WIV sub-monolayer coverage on Si was found to be $Q_\parallel$ independent, suggesting these were localized vibrations of individual WIV particles. Recall the localized frequency $\nu_{\text{loc}}$ of the lowest energy eigenmode for a spherical particle is related to the diameter of the particle $D$ and the transverse sound velocity $V_T$ of the material:\textsuperscript{169}

$$\nu_{\text{loc}} \equiv 0.85 \frac{V_T}{D} \quad \text{(6.1)}$$
Equation 6.1 effectively estimated $V_T$ of PMMA from the lowest and most intense Brillouin mode of PMMA spheres. Here too, equation 6.1 was used to estimate transverse sound velocity from the $Q$-independent mode from WIV. The Brillouin frequencies (average of Lorentzian peaks from Stokes and anti-Stokes modes) and calculated velocities of the $Q_{\parallel}$ independent mode from WIV monolayer and sub-monolayer are listed in Table 4.

Table 4  Brillouin frequencies and velocities of the $Q_{\parallel}$ independent mode from WIV monolayer and sub-monolayer.

<table>
<thead>
<tr>
<th>$Q$</th>
<th>$\nu_T$ (GHz)</th>
<th>$V_T$ (km/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mono</td>
<td>sub-mono</td>
</tr>
<tr>
<td></td>
<td>Mono</td>
<td>sub-mono</td>
</tr>
<tr>
<td>14</td>
<td>8.92</td>
<td>--</td>
</tr>
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<td>17.3</td>
<td>8.77</td>
<td>8.52</td>
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<tr>
<td>20</td>
<td>8.85</td>
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<td>22.1</td>
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<tr>
<td>23.6</td>
<td>8.96</td>
<td>8.34</td>
</tr>
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</table>

Applying equation 6.1 to the WIV ($D = 140 \pm 5$nm) eigenmode at $\nu_{loc} = 8.8 \pm 0.2$ GHz (Figure 101 and Figure 103) yields an average transverse sound velocity $V_T = 1.45 \pm 0.10$ km/s, which is both within the experimental error of our $V_T$ determination from propagating waves in multi-layer WIV and comparable to a hard plastic like PMMA.

The $Q_{\parallel}$ dependence of the all the WIV mode frequencies, as measured on Si, are plotted in Figure 104. WIV frequencies include the propagating modes in the WIV multi-layer assembly and the non-propagating (localized) modes in the WIV monolayer and sub-monolayer coverage. The dashed line through the propagating modes indicates the Rayleigh frequencies used to estimate $V_T = 1.55 \pm 0.10$ km/s from the propagating modes of the WIV multi-layer assembly.

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6.3 Discussion of Wiseana Iridescent Virus Brillouin Spectra

Unexpectedly, propagating modes in virus assemblies were observed, differentiating them from films of polymeric colloidal particles. The apparent strong particle-particle association suggested by these propagating modes is consistent with previous reports indicating difficulty in fabricating uniform, defect-free viral assemblies, especially in comparison to conventional polymer and silica colloids. Close-packed clusters and open aggregate morphology indicates that a reaction-limited association dominates the local morphology of the WIV assemblies. This association provides an important difference between traditional synthetic colloids and biological colloids. The mechanical coupling between virus particles generates assemblies that behave more as a single unit (or film) with local morphological stability and mechanical properties that can
be correlated to larger length scales. Post-assembly processing and overall assembly fidelity is enhanced by the coupling between viruses. Despite the strong association between viruses in the assemblies, site-specific heterogeneous surface chemistry is still individualized; a property that is unattainable with other synthetic materials and holds potential for data storage devices and sensors.

While the Brillouin spectra of viral assemblies provides important information for the use of viruses as device-oriented materials, the properties of individual virus particles provide valuable information to the biological community. Knowledge of the behavior and properties of individual viruses will enhance the understanding of the process by which viruses breach cellular membranes during infection and may provide information leading towards new methods to detect, manipulate, or destroy virus particles.

The Brillouin results for WIV were compared to i) sound velocities and elasticities of the component materials of WIV, namely dsDNA and protein, ii) analytical and numerical estimations based on rule of mixture and finite element analyses, and iii) previous estimates of virus moduli from calculations and nanoindentation experiments. In the following calculations, the average transverse velocity from the localized modes, $V_T = 1.44 \pm 0.10$ km/s, was used as the basis for calculating $V_L$ and $E$ based on assumptions for Poisson’s ratio and density of WIV. These same assumed values were also used to estimate values in Table 5 from limited data in literature. The assumed values for WIV, as well as DNA, were obtained from references containing various experimental determinations of sound velocities, Poisson’s ratios, and densities for DNA and proteins. For consistency, Poisson’s ratio of $\sigma = 0.33$ and density of $\rho = 1.21$ g/cm$^3$ were used for all estimates of DNA and WIV Young’s modulus.
Table 5 compares reported sound velocities and Young’s modulus for crystalline lysozyme, DNA, and PMMA with these estimates for WIV from Brillouin scattering. Notice the transverse velocities of WIV are consistent with what would be expected for a DNA containing virus where the rigidity of a composite core-shell particle is strongly dominated by its DNA core rather than the capsid shell.

Table 5 Comparison of Brillouin derived longitudinal and transverse velocities for WIV to biomolecules of WIV and PMMA colloids.

<table>
<thead>
<tr>
<th>Material</th>
<th>Longitudinal Velocity $V_L$ (km/s)</th>
<th>Transverse Velocity $V_T$ (km/s)</th>
<th>Density $\rho$ (g/cm$^3$)</th>
<th>Young’s Modulus $E$ (GPa)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lysozyme</td>
<td>1.817$^{107,186}$</td>
<td>0.915$^{107,186}$</td>
<td>1.21$^{107,186}$</td>
<td>2.7$^{186}$</td>
</tr>
<tr>
<td>DNA</td>
<td>3.4-3.8$^{188,187}$</td>
<td>1.7-1.9$^b$</td>
<td>~1.21$^{187,188,+}$</td>
<td>9.3-11.6$^{b,d}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.1-1.2$^c$</td>
<td>1.7$^{187}$</td>
<td>4.2-5.0$^{c,d}$</td>
</tr>
<tr>
<td>WIV</td>
<td>2.88 ± 0.20$^b$</td>
<td>1.44 ± 0.10</td>
<td>1.21$^{186}$</td>
<td>6.7$^{b,d}$ -8.9$^{b,e}$</td>
</tr>
<tr>
<td></td>
<td>4.4 ± 0.2$^c$</td>
<td></td>
<td>1.6$^{187}$</td>
<td>7.3$^{c,d}$ -9.7$^{c,e}$</td>
</tr>
<tr>
<td>PMMA</td>
<td>2.78$^{185}$</td>
<td>1.41$^{185}$</td>
<td>1.19$^{185}$</td>
<td>6.34</td>
</tr>
</tbody>
</table>

$^a$ Upper limits of Young’s modulus calculated from ultrasound or hypersound velocities.

$^b$ Estimated by $V_L \sim 2V_T$ for materials with Poisson’s ratio $\sigma \sim 0.33$.

$^c$ Estimated by $V_L \sim 3V_T$ for materials with Poisson’s ratio $\sigma \sim 0.44$.\textsuperscript{188}

$^d$ Using $\rho = 1.21$ g/cm$^3$

$^e$ Using $\rho = 1.7$ g/cm$^3$

$^+$ Lee et al. cited an average density that accounted for voids in the film.

To comment on assumptions of Poisson’s ratio and density assumptions, Table 5 includes ranges of Young’s moduli for various values of density and Poisson’s ratio. Specifically, unpublished results from Lee et al. suggest $V_L/V_T \sim 3$, or a Poisson’s ratio for DNA films of $\sigma = 0.44$.\textsuperscript{188} If $\sigma = 0.44$ is used for WIV instead of $\sigma = 0.33$, the estimate of Young’s modulus increases by ~10% resulting from a 50% increase in $V_L$. Because
Young’s modulus is less sensitive to changes in $V_L$ than to $V_T$ for a given $\sigma$, estimates for $E$ of DNA decrease by ~40% to a range of ~5.9-7.0 GPa.

It is also difficult to know the density of the DNA in the core of the WIV virion. The density of the protein shell, at least, should be close to that of crystalline lysozyme, $\rho = 1.21$ g/cm$^3$. The density of DNA films ranges from $\rho = 1.21$ g/cm$^3$ for hydrated films (~80% H$_2$O) to $\rho = 1.21 - 1.69$ g/cm$^3$ for dry films. Buoyant density experiments determined the density of other iridescent viruses to be $\rho \sim 1.69$. Another consideration, especially for the film structures (multi- and monolayers), is that fibrils should have a much lower density than either core-shell component, introducing spacing between virions and reducing the effective density of the films. In measurements of localized vibrations of silica nanospheres, Lin et al. accounted for an observed 60% decrease in Young’s modulus as density loss from an 11% volume fraction of pores. This suggests that assuming a lower limit of density corrects somewhat for porosity in the film structures. As a composite structure comprising a ds-DNA core and protein shell, the average density and Poisson’s ratio of the WIV are likely intermediate values of the two constituents, which is why a range of densities is reported in Table 5.

To compare our measurements for WIV with previous rigidity studies, Young’s modulus $E$ is determined from the transverse sound velocities using

$$E = \rho V_T^2 \left[ \frac{3V_L^2 - 4V_T^2}{V_L^2 - V_T^2} \right]$$

(6.2)

Here $\rho$ is the average density of a single virion. Overall the local density within the virus is non-uniform, ranging from the internally packaged DNA to the proteins in the capsid shell. Density of proteins such as crystalline lysozyme are reported to be around $\rho = 1.21$
whereas estimates of DNA and DNA protein complexes range from $\rho = 1.21$ g/cm$^3$ to $\rho = 1.69$ g/cm$^3$. Assuming WIV has an outer layer, including lipid bilayer, capsid shell, and surface structure, ~4 nm thick and the radius of the DNA core is ~66 nm, the DNA comprises ~83% of the virion by volume. Depending on the density assumed for DNA, the volume average density ranges from 1.21 to 1.6, yielding an estimate for WIV Young’s modulus between 6.7 and 8.9 GPa. This is a remarkably high stiffness for a material considered to be ‘soft matter’.

To confirm the Brillouin measurements and provide insight into the relative contribution of DNA and protein capsid shell to the overall rigidity of the virus, Sangwook Sihn at The University of Dayton Research Institute calculated the effective modulus of a core-shell sphere. Solutions were obtained i) analytically, using the rule of mixture (ROM) approach and ii) numerically, using the three-dimensional Mori-Tanaka micromechanical method with a dilute strain concentration factor (tensor).

The WIV was modeled as a spherical DNA core surrounded by a proteinaceous capsid shell. In the calculations, the dimensions and properties were taken as follows: radius of DNA core $r_D = 66$ nm, thickness of capsid $t_C = 4$ nm, Young’s modulus of DNA $E_D = 9.3 – 11.6$ GPa, and Young’s modulus of capsid $E_C = 2.7$ GPa, Poisson’s ratios of DNA ($\sigma_D$) and capsid ($\sigma_C$) were $\sigma_D = \sigma_C = 0.33$.

The analytical solution was obtained by applying a constant radial strain on the outer surface of the capsid shell. A rule of mixture (ROM) then leads to an effective bulk modulus of the WIV ($k^*$):

\[
k^* = \frac{k_C k_D}{k_C \sigma_D + k_D (1 - \sigma_D)},
\]  

\[ \text{(6.3)} \]
where \( k_i = E_i / 3 \left(1 - 2\sigma_i\right) \) with the subscript \( i \) representing the \( D \) for DNA and \( C \) for capsid, and \( \phi_D = \left[r_D/(r_D + t_C)\right]^3 \) is the volume fraction of the DNA. The effective Young’s modulus of WIV (\( E^* \)) can then be calculated as

\[
E^* = 3(1 - 2\sigma^*)k^*,
\]

(6.4)

where the effective Poisson’s ratio of WIV (\( \sigma^* \)) is still unknown, but assumed to be 0.33 for consistency with estimates from experiment.

The effective modulus of the WIV was also calculated numerically with a finite element (FE) method and the micromechanics of composites. The numerical model considered a representative volume element (RVE) consisting of three phases of materials: the DNA core, the capsid shell and an arbitrary matrix material surrounding the WIV in the cubic RVE. Including the third matrix phase eases application of boundary conditions to the FE analysis.

Estimates of the effective modulus from both analytical (ROM) and numerical (FEM) methods agree well with each other. Due to the small relative volume associated with the shell, the effective modulus of the core-shell particle is dominated by the modulus of the core. For the core Young’s modulus ranging from 9.3 GPa to 11.6 GPa (expected DNA values, Table 5), the effective Young’s modulus of WIV is predicted to range from 6.8 GPa to 7.9 GPa. These calculations agree well with the experimental observations and demonstrate the effect of dsDNA on effective Young’s modulus of WIV agrees reasonably well with the Brillouin estimates.

Note that the observed frequencies and estimated Young’s modulus from WIV were ~2-3 times greater than predicted by Talati and Jha for a spherical virus particle.\(^{107}\)
This is to be expected because they assumed the entire virus to have elasticity similar to crystalline lysozyme protein, whereas WIV has a much more rigid DNA core.

The modulus estimated for WIV, $E \sim 7$ GPa, is significantly higher than the values reported for some other viruses. A collection of literature results for mechanical properties of other spherical viruses is summarized in Table 6. These estimates from literature were obtained from nanoindentation measurements and finite element analysis of virus particles in fluid. Full and empty refer to virus capsids with and without their genome core, respectively. A Young’s modulus $\sim 1.8$ GPa was initially reported for

Table 6  Compilation of literature studies for approximately spherical virus particles (via nanoindentation and finite element analysis) for comparison with our estimates for Young’s modulus of the ds-DNA WIV.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Virus</th>
<th>Size, Genome</th>
<th>Spring Constants (N/m)</th>
<th>Young’s Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ivanovska et al.</td>
<td>Empty $\phi 29$ bacteriophage</td>
<td>54x42nm HxW, dsDNA</td>
<td>Bimodal: 0.16 and 0.31 N/m</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>(corrected to 4.5)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Michel et al.</td>
<td>Full &amp; Empty CCMV</td>
<td>28nm OD, 3.8nm shell, 4 ssRNAs</td>
<td>Empty 0.15, 0.19 Full 0.2-0.3</td>
<td>0.14-0.19</td>
</tr>
<tr>
<td></td>
<td>(corrected to 0.28-0.36)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrasco et al.</td>
<td>Full &amp; Empty MVM</td>
<td>25nm OD, ssDNA</td>
<td>Empty ~0.58 Full 0.6, 0.8, 1.4 along 5, 3, and 2 fold symmetry axes</td>
<td>Empty ~1.25</td>
</tr>
<tr>
<td></td>
<td>Full - as high as ~3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kol et al.</td>
<td>Mature &amp; Immature MMLV</td>
<td>~85nm diameter, ssRNA</td>
<td>Immature: 0.68 Mature: 0.31</td>
<td>Immature: 0.233</td>
</tr>
<tr>
<td></td>
<td>Mature: 1.027</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hartschuh et al.</td>
<td>Full WIV</td>
<td>140nm, dsDNA</td>
<td>Sound velocities (km/s)</td>
<td>$\sim 6.7-8.9^a$</td>
</tr>
<tr>
<td></td>
<td>$V_l = 2.88$</td>
<td></td>
<td>$V_t = 1.44$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Using $\sigma = 0.33$ for a density range $\rho = 1.21 – 1.69 \text{ g/cm}^3$

bacteriophage $\phi 29$ virus containing DNA. The later publication by Gibbons and Klug corrected this estimate to $E \sim 4.5$ GPa after accounting for a finite shell thickness,
indenter geometry, and non-linear force responses. They also corrected estimates for CCMV, approximately doubling E to the range 280-380 MPa. Similar corrections to the other data may also result in higher estimates of Young’s modulus.

Notice from Table 6 the similarities and differences between WIV and other viruses for which mechanical properties were measured. Investigating these factors gives some insight to the unusually high Young’s modulus observed for WIV. The discrepancy between our data for WIV and earlier estimates for a couple of other viruses is outside the uncertainty associated with approximation error and might have a few reasons.

i) The first difference to note is that of time scale of the measurement techniques. Brillouin spectroscopy measures hypersonic acoustic wave velocity associated with high frequency (GHz) modulus, whereas nanoindentation measures nearly static spring constants, a difference of nine orders in frequency. The rigidity of viscoelastic materials exhibits substantial rate dependence, effectively being harder at higher rates of deformation. For example, PMMA is reported to have a Young’s modulus of 3.3 GPa when measured at 10 Hz and 6.3 GPa when measured at GHz frequencies. This difference is associated with relaxation processes that occur in the frequency range between these two measurement frequencies.

ii) The second factor leading to a higher modulus is the fact that WIV is much larger (2-5 times) than φ29, CCMV, MMV, or MMLV. Thus, WIV has a larger genome core than the smaller virions. However, the volume fraction of dsDNA in WIV is very similar to the smaller dsDNA virus φ29, because the capsid thickness of φ29 is only ~1.6 nm compared to ~4 nm for WIV. Following the rule of mixture (ROM) model, the ds-DNA core of WIV makes up ~83% of the total virion volume compared to ~81% for φ29.
(assuming a spherical shape with radius 48 nm). Thus the ROM estimate predicts roughly the same modulus for \( \phi 29 \) as for WIV.

iii) The extent of hydration has a considerable influence on compliance, as commonly observed for biological structures. Thus our measurements performed at low levels of hydration might probe viruses that are much harder than the ones measured in solutions.\(^{101,102,103}\)

iv) In general, RNA viruses seem to be softer than their ds-DNA counterparts (see Table 6). Interestingly, the empty capsids of a RNA virion have lower spring constants than empty capsids of a DNA virion. It seems that nature has developed a shell for DNA capsids capable of withstanding the exceptional internal pressures of highly packed virial DNA,\(^{105}\) which is much stronger than that of virial RNA.

Direct comparison of nanoindentation and Brillouin measurements performed on the same virus in similar conditions will help to sort out possible reasons for the observed difference in the modulus estimates.

6.4 Summary of Results from Wiseana Iridescent Virus

In summary, Brillouin spectroscopy was shown to be an effective non-contact and non-destructive method to measure the mechanical properties of viruses and their assemblies. At least for spherical viruses, Brillouin may complement alternative probe techniques such as nanoindentation for single virion rigidity. The results presented here also demonstrate strong mechanical coupling between individual WIV particles and their surprisingly high modulus \(\sim 7\) GPa. Mechanical modeling confirmed that the hard DNA
core dominates the modulus. Brillouin spectroscopy might find broad application in analysis of mechanical properties of biological structures and other soft materials assemblies, their dependence on environment and interactions. Furthermore, knowledge of the mechanical properties of viruses and their assemblies, and knowledge of their vibrational eigenmodes might help to model drug and gene delivery processes, to address some anti-viral therapy approaches, define processing limitations of viral nano-templates/devices and provide insight into the dynamic behavior of viruses throughout their lifetime.
CHAPTER VII

SUMMARY

Brillouin light scattering was used to measure mechanical properties of nanostructured materials. These studies extended Brillouin from a characterization method for thin films to a metrology for more complex two- and three-dimensionally confined polymeric, inorganic, and biological structures. By measuring propagating and localized acoustic vibrations, Brillouin scattering is a powerful tool for non-contact, non-destructive analysis of elastic constants for nanoscale materials.

Lithographically prepared photoresist polymer grating lines in Chapter IV provided well-defined samples to evaluate phonon spectra as they relate to moduli in two-dimensionally confined structures. The grating structures resulted in new Brillouin modes not observed for uniform films. In particular, a low-frequency wave was observed that was unexpected for supported films. Classic wave theory and finite element analysis were combined to identify this new mode as a flexural vibration of the grating lines. Analysis of the phonon spectra provided estimates of elastic constants in the nanostructures and indicated no significant deviation from bulk mechanical properties and no mechanical anisotropy in structures as small as 88 nm.

From first approximations, non-propagating vibrations yielded similar elastic constants as propagating waves in 88 nm wide polymer and 112 nm wide silicon oxide
(SiO$_x$) grating lines. Low frequency shear vertical phonons propagating across SiO$_x$ grating lines were slightly or completely damped compared to analogous modes propagating parallel to the grating lines. In polymer grating lines, phonon propagation perpendicular to the grating lines was even more significantly damped. Strong differences between elastic constants of the grating lines and the substrate lead to strong localization of modes and no propagation from one line to another. In general, though limited analysis could be applied to high frequency Brillouin modes from the grating lines, low-frequency propagating modes and most localized modes from the grating lines were related to shear or longitudinal moduli.

Non-propagating vibrations from assemblies of poly(methyl methacrylate) (PMMA) spheres were observed and related to transverse sound velocity. The Brillouin spectra from the 300 nm diameter particles resulted in transverse velocity, and thus shear modulus, comparable to bulk PMMA, as expected for particles much larger than molecular dimensions. Biological spheres, Wiseana Iridescent Viruses (WIV), were assembled in layers of various thicknesses and surface coverages. In contrast to PMMA spheres, the Brillouin spectra of WIV assemblies revealed propagating acoustic waves. These propagating modes were indicative of strong mechanical coupling between the virus particles, perhaps through the fibrillar structures extending from the capsid shell. A transverse velocity $V_T = 1.55 \pm 0.10$ km/s was estimated from the short wavelength “film-like” phonons.

Brillouin scattering from isolated WIV particles showed a non-propagating mode. Treated as a spherical resonance, the transverse velocity of this mode was estimated to be $V_T = 1.44 \pm 0.10$ km/s. Both WIV assemblies and individual WIV particles seem to be
much more rigid than models of viral vibrations or elasticities that assume viruses to have elastic properties similar to the protein lysozyme ($V_T \sim 0.9$ km/s). Rather, the WIV Brillouin studies suggest that the DNA core, and not the protein shell, of WIV dominates the Young’s modulus. Due to uncertainties in density, estimates fall within the range $E_{\text{WIV}} \sim 6.7 – 8.9$ GPa. This range of values for Young’s modulus is slightly higher than values obtained from nanoindentation and finite element analysis even after correction for non-linear force responses.

Moving forward in the development of new and miniaturized components in the age of nanotechnology, Brillouin spectroscopy could find applications for probing elastic constants of nanostructured materials beyond simply thin films. Brillouin can be applied to situations in which the geometries and boundary conditions are well-known such that the phononic spectrum can be estimated analytically or numerically, as was the case for these studies of lithographically prepared nanolines and spherical-like virus particles. A near future application may be nanoimprinted nanolines with dimensions reaching the regime in which deviations from bulk properties are expected.
REFERENCES


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APPENDICES
APPENDIX A

MATHEMATICA NOTEBOOK EQUATION 2.29

(* Determinant for a film on substrate
from G.W. Farnell and E.L. Adler, p. 48, Eq. 18 *)
y = 6.28 (*y = kh = Qd*)
vl = 2.4 (*VL Layer: Photoresist = 2.4,
SiOx = 5.95, PS = 2.323, Lysozyme crystal = 1.817*)
vt = 1.29 (*VT Layer: Photoresist = 1.29,
SiOx = 3.74, PS = 1.147, Lysozyme = 0.915*)
Clear[b5, b6, bc, bd, r, m]
b5 = I*(1 - x^2/vt^2)^0.5
b6 = I*(1 - x^2/vl^2)^0.5
c1 = 5.95 (*VL Substrate: Si = 8.94, SiOx = 5.95, Al = 6.42, Float Glass = 5.85*)
ct = 3.74 (*VT Substrate: Si = 5.34, SiOx = 3.74, Al = 3.04, Float Glass =3.47*)
bc = -I*(1 - x^2/ct^2)^0.5
bd = -I*(1 - x^2/c1^2)^0.5
r = 2.2*ct^2/(1.056*vt^2)
(calculated from sound velocities via densities Si = 2.33,
Silicon oxide = 2.2, PS = 1.056, Al = 2.7, Lysozyme crystal = 1.21*)
rl = 66.44/1.39 (* Not used in m;
    ratio of c44 of substrate to layer; here = c44(Si)/c44(PS) *)

m = {(b5, -1, -b5, -1, -bc, 1), (-1, -b6, -1, b6, 1, bd),
{1-b5^2, 2*b6, 1-b5^2, -2*b6, -r*(1-bc^2), -2*r*bd},
{2*b5, -1+b5^2, -2*b5, -(1-b5^2), -2*r*bc, r*(1-bc^2))},
{(1-b5^2)*Exp[I*y*b5], 2*b6*Exp[I*y*b6], (1-b5^2)*Exp[-I*y*b5],
-2*b6*Exp[-I*y*b6], 0, 0}, {2*b5*Exp[I*y*b5], -(1-b5^2)*Exp[I*y*b6],
-2*b5*Exp[-I*y*b5], -(1-b5^2)*Exp[-I*y*b6], 0, 0}]

Plot[{Det[m], {x, 0, 3}} Plot[{Det[m], Im[-Det[m]]}, {x, 0, 3}]
FindRoot[Det[m] = 0, {x, 1.2}]

6.28
2.4
1.29

192
\[ i (1 - 0.600925 x^2)^{0.5} \]
\[ i (1 - 0.173611 x^2)^{0.5} \]
5.95
3.74
\[-i (1 - 0.0714919 x^2)^{0.5}\]
\[-i (1 - 0.0282466 x^2)^{0.5}\]
17.5115
47.7986

\[ \{i (1 - 0.600925 x^2)^{0.5}, -1, -i (1 - 0.600925 x^2)^{0.5}, -1, i (1 - 0.0714919 x^2)^{0.5}, 1\}, \]
\[-1, -i (1 - 0.173611 x^2)^{0.5}, -1, i (1 - 0.173611 x^2)^{0.5}, 1, -i (1 - 0.0282466 x^2)^{0.5}\}, \]
\[ \{1 + (1 - 0.600925 x^2)^{1}, 2 i (1 - 0.173611 x^2)^{0.5}, 1 + (1 - 0.600925 x^2)^{1}, \]
\[-2 i (1 - 0.173611 x^2)^{0.5}, -17.5115 (1 + (1 - 0.0714919 x^2)^{1})\}, \]
\[35.0229 i (1 - 0.0282466 x^2)^{0.5}\}, \{2 i (1 - 0.600925 x^2)^{0.5}, \]
\[-1 - (1 - 0.600925 x^2)^{1}, -2 i (1 - 0.600925 x^2)^{0.5}, -1 - (1 - 0.600925 x^2)^{1}, \]
\[35.0229 i (1 - 0.0714919 x^2)^{0.5}, 17.5115 (1 + (1 - 0.0714919 x^2)^{1})\}, \]
\[e^{6.28 (1-0.600925 x^2)^{0.5}} \{1 + (1 - 0.600925 x^2)^{1}, 2 i e^{6.28 (1-0.173611 x^2)^{0.5}} \}
\[(1 - 0.173611 x^2)^{0.5}, e^{6.28 (1-0.600925 x^2)^{0.5}} (1 + (1 - 0.600925 x^2)^{1})\}, \]
\[-2 i e^{6.28 (1-0.173611 x^2)^{0.5}} (1 - 0.173611 x^2)^{0.5}, 0, 0\}, \]
\[2 i e^{6.28 (1-0.600925 x^2)^{0.5}} (1 - 0.600925 x^2)^{0.5}, e^{6.28 (1-0.173611 x^2)^{0.5}} \]
\[(-1 - (1 - 0.600925 x^2)^{1}), -2 i e^{6.28 (1-0.600925 x^2)^{0.5}} (1 - 0.600925 x^2)^{0.5}, \]
\[e^{6.28 (1-0.173611 x^2)^{0.5}} (-1 - (1 - 0.600925 x^2)^{1}), 0, 0\} \]

Plot::plnr : -Det[m] is not a machine-size real number at x = 1.384988862671059. More...
Plot::plnr : -Det[m] is not a machine-size real number at x = 1.3215342323018368. More...
Plot::plnr : -Det[m] is not a machine-size real number at x = 1.3049188570889925. More...

General::stop : Further output of Plot::plnr will be suppressed during this calculation. More...
[x \to 1.20867 + 0.\,i]
APPENDIX B

MATHEMATICA NOTEBOOK EQUATION 2.34

RAYLEIGH MODE (Farnell & Adler, p. 57), as $kh \to \infty$

Clear[x] (* $X = (VR/VL^2)$ *)
vl = 5950 (*layer velocities*)
vt = 3740

$b = (vl/vt)^2$.

FindRoot[$(2 - b x)^2 = 4 ((1 - x) (1 - b x))^{(1/2)}, \{x, 0.2\}$]

5950

3740

2.53099

{x -> 0.324582}

$vl = \sqrt{0.324582}$ (* $VR =$ *)

3389.84
APPENDIX C

MATHEMATICA NOTEBOOK EQUATION 2.35

ANTISYMMETRIC LAMB WAVE: \( a = k h, \ b = (vl/\nu t)^2 \)

\[
\begin{align*}
\text{b5} & = \nu \sqrt{1 - (\nu / \nu t) \ ^2} \ ; \ \text{b6} = \nu \sqrt{1 - (\nu / \nu l) \ ^2} \\
& = \sqrt{1 - \frac{\nu^2}{\nu l^2}} \nu \\
\text{Clear} \{x\} \\
\text{Clear} \{b\} \\
\text{Table}[
\{a, \text{FindRoot} \{\text{Tanh}[a/2 \cdot (1-x) \ ^{(1/2)}] = 4 ((1-x) \ (1-b \ x)) \ ^{(1/2)} / (2-b \ x) \ ^2 \\
\text{Tanh}[a/2 \cdot (1-b \ x) \ ^{(1/2)}] / . b \rightarrow 2.2, \ {x, .271}\}, \ {a, 1, 10}\}]
\end{align*}
\]

(*SAME RESULTS AS FIRST MODE FROM DETERMINANT EVALUATION; APPENDIX A*)

\[
\begin{align*}
\{1, \ {x \rightarrow 0.0643504}\}, \ {2, \ {x \rightarrow 0.161088}\}, \ {3, \ {x \rightarrow 0.230124}\}, \\
{4, \ {x \rightarrow 0.274546}\}, \ {5, \ {x \rightarrow 0.303186}\}, \ {6, \ {x \rightarrow 0.321988}\}, \ {7, \ {x \rightarrow 0.33453}\}, \\
{8, \ {x \rightarrow 0.342979}\}, \ {9, \ {x \rightarrow 0.34869}\}, \ {10, \ {x \rightarrow 0.352541}\})
\end{align*}
\]
APPENDIX D

MATHEMATICA NOTEBOOK EQUATION 2.36

LOVE MODES (Farnell & Adler, p. 67)

\[ \text{bs} = v^2 = x \cdot v \cdot l^2 \] (layer); \[ \text{xs} = \text{substrate} 1/Vt^2, \text{vt(layer)} \cdot <v<\text{vt(substrate)}; \]
\[ r = \text{substrate} c44 / \text{layer} c44; \]
\[ \text{vt(layer)} < v < \text{vt(substrate)} \]

\text{Clear}[x]

a = 10
b = 5.95^2 / 3.74^2
vl = 5.95
xs = 1 / 28.5156
r = 2.33 \cdot 5.34^2 / (2.2 \cdot 3.74^2)

\text{FindRoot}[\text{Tan}[a (b x - 1) ^ (1/2)] =
\{ r (1 - x vl^2 xs) ^ (1/2) / (b x - 1) ^ (1/2), \{x, 0.57}\}]

10

2.53099

5.95

0.0350685

2.1591

\{x \rightarrow 0.603494\}
APPENDIX E

LINEWIDTH VS. EXPOSURE DOSE

![Graph showing linewidth vs. exposure dose]
- 150, 120 and 110 nm should show up at 21-23 mJ/cm²
- 100 nm should show up at 22-24 mJ/cm²
- 90, 80 nm are typically not resolved
Proposed Binary Mask for 0.68 NA
193 nm ASML Tool

CA = Contact
1:1 = 1:1.1 s
1:2 = 1:2.1 s

Wafer plane dimensions
Chip size 26 mm X 32 mm

• Lines should be 10 microns long with 1 micron spacings
• Design specifically for AFM resist sidewall roughness measurements
Within Each 4 mm Square...

- Introducing a single offset within each sub-chip ensures good SEM cross-sections.