PHOTOMECHANICAL ACTUATOR DEVICE BASED ON DISPERSE RED 1
DOPED POLY(METHYL METHACRYLATE) OPTICAL FIBER

By

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A dissertation submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

WASHINGTON STATE UNIVERSITY
Department of Physics and Astronomy

DECEMBER 2013

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ACKNOWLEDGMENTS

First and foremost, I would like to thank my supervisor Professor Mark G. Kuzyk, the wizard of light, for giving me the opportunity to enrich myself between fascinating optical research topics, from optical tweezers to photomechanics, and for his vast knowledge on optics and other aspects of life which has been a great inspiration to me.

I would like to thank my research committee: Professors Matthew D. McCluskey for generously allowing me to use the PVD apparatus, Peter W. Engels for his willingness to listen and help, Yi Gu for providing me access to the testing instruments and software in the Electronics Lab. I thank Professor John B. Schneider at EECS of WSU, for his numerical computation class providing me the necessary programming skill to tackle my research problems.

I also want to thank my present and past office mates, Mr. Shengting Hung, Dr. Nathan Dawson, and Dr. Shiva K. Ramini, for sharing stories and jokes when research was tossed aside. I thank all the members of the group for making the nonlinear optics lab a wonderful working place, and all other people who have offered help during my stay at WSU.

I thank Department of Physics and National Science Foundation for their generous funding support in various forms such as Teaching assistantship, Millennium fellowship, and research grants.

Last, I’d like to thank my family for their great patience and endless support during these years.
PHOTOMECHANICAL ACTUATOR DEVICE BASED ON DISPERSE RED 1
DOPED POLY(METHYL METHACRYLATE) OPTICAL FIBER

Abstract

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December 2013

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The photomechanical effect is the phenomenon involving any mechanical property change of a material induced by light exposure. Photomechanical devices can be built with superior performance over traditional devices and offer versatile control tactics.

Previous experiments show that disperse red 1 azobenzene (DR1) doped poly(methyl methacrylate) (PMMA) optical fiber has a fast photomechanical response upon asymmetrical 633nm laser irradiation originating in photoisomerization of the dopants between the cis and trans forms, which causes an elongation of the polymer fiber. In this work, laser light of 355nm wavelength is used to investigate the dynamics of the trans to cis photoisomerization process, which should result in length contraction of the DR1 doped PMMA polymer fiber. A three-point-contact optically-actuated beam controlling tilt mount is made and used as the measurement apparatus to study this process. The photomechanical fiber is observed to elongate upon UV irradiation.
Numerical simulations, which take into account the coupled effect between the laser-induced temperature increase and population density change of the dye molecules, show that contraction of the fiber due to direct trans-cis photoisomerization is overwhelmed by elongation due to the photo-thermally-stimulated cis-trans isomerization under high intensity. An ink coated entrance face of the fiber is placed in the measurement tilt mount and is found to exhibit contraction in the fast process under low intensity without sacrificing the good signal to noise ratio enjoyed in the high intensity case.
DEDICATION

TO MY PARENTS

HUAQING YE AND LIANZHI CHENG
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Chapter 1

Introduction

A photomechanical effect is a change of the physical properties of a material induced by light irradiation[2]. The most common physical changes include material density and shape. A variety of potential applications can be made based on photomechanical response (magnitude and spectral response) depends on the mechanisms. This dissertation seeks to characterize dye-doped polymers so that the mechanisms can be determined and device applications made practical, including photomechanical actuators.

1.1 Motivation

An actuator is a device which most commonly utilizes a controlled shape change caused by external stimuli of physical or chemical origin such as mechanical, thermal, electrical as well as some other novel actuation causes including piezoelectric and photomechanical effects[3]. Devices based on the photomechanical effect can have superior performance over conventional mechanical actuators, which often suffer from drawbacks such as low positioning accuracy, low mechanical stability, mechan-
ical vibration, backlash, loud operation as well as bulky form factor. Piezoelectric actuators, which are based on the conversion between mechanical and electrical energy, can also operate with high positioning accuracy and mechanical stability, but often are expensive. Also, sophisticated drive systems are often required to overcome backlash. Tethered operation presents a significant limitation on its potential for miniaturizing[3]. The inconvenience of generating an arbitrarily distributed electric field makes it difficult to create smart shape changing materials. The need of high voltages and the pronounced nonlinear hysteretic behavior in the presence of comparatively high electric fields further restrict the reuse of applications[4].

In contrast, photomechanical devices can be highly stable and operate silently with fast response and high precision in environments that cannot tolerate electromagnetic interference. They can achieve non-tethered operation in hard-to-reach places without external wiring. They can also be built into ultra small form factor at an affordable price, which makes them good candidates for building optical circuitry, miniature sensor/actuator arrays (e.g., deformable mirror, spatial light modulator), lab-on-chip devices and many other size-demanding applications. Photomechanical actuation can be achieved through versatile control schemes including the use of intensity, wavelength, polarization[5], beam profile (as required rigorously in typical optical tweezers experiments) and other properties of light, as well as by manipulating the location of the light-sensitive moieties within a polymer matrix[6].

1.2 Previous Work

The earliest experiments on the photomechanical effect can date back to 1881 when Alexander Graham Bell used the opto-acoustic effect to produce sound in a gas with a chopped beam of sunlight[7]. In the 1980s, an optically controlled fluidic actuator[8]
and the optical heating of a closed gas-filled volume, which was employed to move a flexible diaphragm in a flapper nozzle device[9], were demonstrated. In 1990, direct optical to mechanical actuation was performed by laser-induced deflection of the fluidic supply jet flow[10]. Recently, due to the rapid development of materials research, the photomechanical effect has been widely demonstrated in beams, plates, and films[5, 11, 12, 13, 14], and in structured surfaces to make light-actuated swimmers[15] enhanced by the use of liquid crystal elastomers[16, 17, 18]. Glassy dye-doped polymers possess high optical quality and the ability to be drawn into long optical fibers, which is an important advantage over lower-quality materials such as liquid crystal elastomers, and makes possible the design and fabrication of cascaded waveguiding device structures. However, little effort has been devoted to dye-doped polymer optical fibers in the wave-guiding geometry. While the photomechanical response of a glassy dye-doped polymer is generally faster than that of a liquid-crystalline elastomer, the photomechanical response of liquid-crystalline elastomers is generally an order of magnitude larger than that of glassy dye-doped polymers. However, the limitation of lower optical quality makes elastomers better suited for non-waveguiding applications.

The first demonstration of the photomechanical effect in a PMMA polymer fiber in the waveguide geometry was made by Welker and Kuzyk who then used it to make an all-optical feedback circuit that acted as a highly accurate position stabilizer with active vibration suppression[19]. Though the photomechanical effect in a glassy polymer is small, the use of a fiber waveguide geometry to increase the interaction length and intensity, and, interferometry to leverage the device’s sensitivity, made the device fully operational with impressive specs[19].

In 1997, Welker and Kuzyk demonstrated active vibration suppression of a plastic sheet with the use of an integrated Fabry-Perot mesoscale photomechanical unit[20].
In 2006, Bian et al. reported direct observation of bending of a DR1-doped PMMA polymer fiber cantilever under 633nm off-axis laser illumination, which was found to result from cis-to-trans photoisomerization[21]. In 2011, Dawson et al. investigated photomechanical response in liquid crystal elastomer optical devices, which concluded that photothermal heating is the dominant mechanism[22, 23].

Recently, several DR1-doped PMMA polymer fiber based photomechanical structures have been made, including two Fabry-Perot interferometer designs and a photomechanical tilt mount[1], the latter of which is used as the photomechanical measurement apparatus to study the dynamics of the tran-cis photoisomerization mechanism by using on-axis illumination at the fiber end-face, in contrast to typical liquid crystalline polymer experiments which usually use side illumination[24].

### 1.3 Mechanisms

Various mechanisms can contribute to the photomechanical effect. Below is a description of the more common photomechanical mechanisms which have been widely observed by experimental techniques that are able to deconvolute the mechanisms[2].

#### 1.3.1 Photothermal Heating

Thermal expansion is a universal physical property of materials, and particularly large in polymeric thermoplastics. Rapid heating by laser light can raise the temperature of a polymer dramatically in a short time, which tends to result in a noticeable change in its physical dimensions, e.g., shape and length. Depending upon the laser heating schemes and thermal properties of a material, elongation, contraction, and bending can result. Photothermal heating in an optically dense material is a non-local effect in that heat diffuses from the illuminated area to dark regions, inducing length
changes where light is absent. The temperature profile follows the laser intensity profile when the laser is first turned on, which results in a strain that follows the intensity profile[2]. An example of a practical application of the mechanism is Welker’s all-optical feedback circuit[19].

1.3.2 Photostriction

Photostriction is the phenomenon of light-induced mechanical strain. An interface between two materials becomes charged when the two materials are differentially polarized. An electric field gradient that forms at an interface in response to an applied electric field, will exert a net force on the dipolar induced charge at the surface and perpendicular to it[2]. Photostriction can also be described as the combination of the photovoltaic and the converse piezoelectric effect[13]. The photovoltaic effect is the conversion of light radiation into an electric field, and the piezoelectric effect in the material converts electric field into mechanical strain. Materials with a large photostrictive effect, such as the artificially engineered PLZT ceramics (Lanthanum-modified Lead Zirconate Titanate), have been used to make a micro walking device that is powered solely by light[13].

1.3.3 Photoreorientation

When polar molecules are placed in an electric field, the field exerts a torque on the dipole moment of the molecule. The net effect of this torque is to rotate the molecule until its dipole moment is aligned along the direction of the applied field as shown in Figure (1.1). When polarized light interacts with a material, dipole moments are induced within the molecules making up the material. The dipole moments then tend to align with the polarization of light. Such molecular reorientation in a solid results
in internal stress that can macroscopically deform the material. Photoinduced reorientation is often an important mechanism in liquid crystalline polymers since they can be specifically engineered so that mesogen reorientation leads to a phase transition from the nematic to the dissociated phase, thus leading to a huge bulk change in the material’s mechanical properties[25]. Mesogens can be covalently attached to a polymeric matrix to enhance the effect. Alternatively, a dye-doped polymer has a photomechanical response due to steric interaction between the dopant molecules that change shape and the host polymer.

Photoinduced reorientation in azobenzene-group-containing materials is most often based on photoisomerization[26]. Under the illumination of linearly polarized light, photoisomerization activates chromophores whose transition dipole moment has a component along the light polarization and causes the molecules to on average reorient away from the light’s polarization[25]. Excluded from optical activation, molecules perpendicular to the light’s polarization will be unaffected, so the transverse chromophore population will grow. The trans-cis-trans photoisomerization cycle can result in rotational diffusion of the molecules from their initial alignment.

\[
\vec{p} = q \vec{d}
\]

Figure 1.1 Photoreorientation

Photoinduced reorientation in azobenzene-group-containing materials is most often based on photoisomerization[26]. Under the illumination of linearly polarized light, photoisomerization activates chromophores whose transition dipole moment has a component along the light polarization and causes the molecules to on average reorient away from the light’s polarization[25]. Excluded from optical activation, molecules perpendicular to the light’s polarization will be unaffected, so the transverse chromophore population will grow. The trans-cis-trans photoisomerization cycle can result in rotational diffusion of the molecules from their initial alignment.
1.3.4 Photoisomerization

Photoisomerization is the process in which atoms in a molecule change geometric structure upon light irradiation without changes in chemical structure. Stilbene and azobenzene containing molecules are typically found to come in at least two isomorphic forms. This class of compounds normally have at least one C=C or N=N double bond within its chemical structure. Figure (1.2) shows a reversible isomerization process between trans (or E) and cis (or Z) isomers, through either one-bond-flip or twist[27]. The cis isomer has chemical groups on the same side of the double bond resembling a folded shape, while the trans isomer has chemical groups on the opposite sides giving a more stretched shape.

![Figure 1.2 Trans – Cis Isomerization](image)

Figure (1.3) shows the energy diagram of bonding, which outlines six possible electronic transitions between different molecular orbitals. Of the six, only the two lowest energy transitions can be excited by absorbing photons in the 200 to 800nm region, i.e., n → π* and π → π*. UV light is absorbed by oxygen in air and quartz glass, so excitations to light below 200nm is not normally observed. Thus the normal ultraviolet-visible spectroscopy in the 200 to 800nm range only sees these two transitions.

Azobenzene photoisomerization has been extensively studied over the past few decades due to its reversibility and because it is free from side reactions[28]. During
the last century, intense research was devoted to characterize its isomers and to understand their properties. The earliest investigation can be traced back to the 1930s when Hartley made the first discovery of the cis form of azobenzene in solution exposed to sunlight[29]. In the 1950s, Fischer et al. carried out a series of experiments that indicated that the composition of trans and cis isomers in photoisomeric equilibrium depended on the illumination wavelength and the cis isomer concentration was maximized at 365nm illumination[30]. Later, Zimmerman further showed the photostationary composition only depended on the illumination wavelength, regardless of initial composition and light intensity[31]. In 1960, Fisher found in his temperature dependence experiment that, in the absence of thermal isomerization, the photoequilibrium shifts towards the trans isomer upon cooling, and the quantum yields of photoisomerization has a strong dependence on temperature[32]. In the 1980s, Eisenbach observed a reversible contraction and expansion in azo-aromatic crosslinked polymer films, mainly due to the conformational change of the azo dye[33]. In the 1990s, Sekkat et al. demonstrated the photoisomerization of disperse red 1(DR1) in PMMA thin films[34]. Under UV irradiation, the trans-DR1 molecule converts to a cis-DR1 molecule. Under visible irradiation, the reverse cis to trans isomerization...
occurs. The cis isomer can also undergo thermal relaxation, back to the trans form. The reversible process is shown in Figure (1.4).

![Photoisomerization of Disperse Red 1](image)

**Figure 1.4** Photoisomerization of Disperse Red 1

The mechanism of photoisomerization of azobenzene still remains controversial. The debates concern the two possible pathways. The first probable explanation is through the rotation of the activated N-N single bond, which requires the breaking of the π bond[35]. The second is inversion with the π bond intact, which requires less energy than bond breaking. Both mechanisms are observed in different chromophores and environments[36, 37].

### 1.3.5 Photomechnics in Human Eye

The photomechanical effect is found in the human body, and it is most notable in human vision[38, 39]. The primary step in human vision is the photoisomerization process of the photosensitive chromatophore group, i.e., the retinal molecule, bound within a chromoprotein, called opsin, together forming rhodopsin. The retinal molecules have several different conjugated double bonds, which are all in trans form except for one in the cis conformation. The retina contains two types of photoreceptors, called rods and cones. Rod cells all absorb the same wavelength at 500 nm, which is responsible for black and white vision. Humans have three types of cones, each having a different absorption band in the visible range centered at 455nm (blue-
absorbing), 530 nm (green absorbing), and 625 nm (red-absorbing). Thus the cones are responsible for color vision. All known animal photoreceptors use retinal as the chromophore, which gives it its color. When light is absorbed by a photopigment, the **11-cis** form of retinal, which has a folded shape, undergoes a conformational change to the **all-trans** form which has a straighter shape as shown in Figure (1.5). This change in retinal’s shape initiates a chain of events which eventually leads to a nerve impulse transmitted to the brain, forming a visual image. The **all-trans** retinal form then isomerizes back to the **cis** form by an enzyme in the absence of light exposure, which makes the entire process reversible[40].

![Figure 1.5 Photoisomerization in human vision](image)
Chapter 2

Device Fabrication

2.1 Introduction

In this chapter, we discuss the fabrication of three different photomechanical structures. Figure (2.1) shows a schematic diagram for them. All structures require the fabrication of a dye-doped fiber, coating of microscope coverslips to make them reflecting, polishing of the fiber component to allow for good fiber coupling, and assembling of the components to make the final structure.

Figure 2.1(a) shows the original design, which consists of three polymer fiber supports and two silvered partially reflective microscope coverslips, forming a Fabry-Perot interferometer (FPI). Section 2.4.2 describes the assembly process. The photomechanical response of this FPI is to be measured by probing the interference fringe shifts upon pump irradiation. Figure 2.1(b) is an improved version of the interferometer but with two fiber supports replaced by very fine miniature mechanical springs made from copper, leaving one fiber available for actuation. Figure 2.1(c) shows a photomechanical tilt mount made of two fine copper wire C legs. The photomechanical response is strong enough to be detected by a position sensitive detector that records
the deflection of a beam reflected from the upper silvered glass coverslip, shown in blue in Figure 2.1(c). Section 2.4.3 describes the assembly process of this device.

2.2 Polymer Fiber Drawing

The dye-doped polymer fiber used in this work is fabricated by a custom made fiber drawing tower in our laboratory located in the clean room shown in Figure 2.2. Details regarding polymer fiber fabrication can be found in previous group publications[41, 42, 2]. In general, a fiber is made in three steps:

- Dye-doped polymer preparation;
- Core-preform fabrication;
- Fiber drawing.

Fiber used in this work is made by dissolving 0.5% Disperse Red 1 dye by weight into MMA monomer with initiator, which mediates the polymerization process and chain transfer agent, which controls the average chain length. The solution is then transferred into test tubes, which are subsequently placed in an oven set to a temperature of 95°C for 7 days to drive the polymerization reaction. The test tubes are capped during the process but periodically uncapped to release pressure and prevent bubbling. Then, the preforms are removed from the test tubes and mounted into a squeeze assembly at elevated temperature to further remove residue gases and further compress the material to remove voids. Then, preforms are mounted on the fiber drawing tower to pull fiber. The typical diameter of the fiber used in this work is 475µm.
Figure 2.1 Three different designs of photomechanical devices[1]
Figure 2.2 Fiber drawing tower. (1) Preform feed translation stage. (2) Oven. (3) Variac to oven coils. (4) Cool-down oven. (5) Take-up speed control. (6) Tension gauge. (7) Preform feed control. (8) Tension sensor system. (9) Take-up spool. (10) Take-up spool translation stage.
2.3 Physical Vapor Deposition

2.3.1 Introduction

Partially reflective mirrors are made by evaporating aluminum or silver onto glass substrates such as microscope glass slides and coverslips using the physical vapor deposition (PVD) technique. This section will detail the operation of this apparatus since it was not mentioned previously.

The PVD apparatus consists of a deposition chamber, vacuum pumps and a control tower. The vacuum deposition chamber is a bell jar enclosed by a shielded cage. The evaporation source is a thin folded tungsten boat, shown in Figure 2.3, which holds a small amount of coating material in the form of chunks in its trough. Once the chamber reaches the required deposition pressure, an electrical current of 196A is passed through the boat, thermally vaporizing the coating material with a typical temperature of 1800°C. When reaching the glass substrate mounted at the upper location inside the chamber, the vapor condensates back to the solid state, forming a thin film layer.

![Figure 2.3 Tungsten boat](image)

This deposition apparatus is equipped with a mechanical pump, a cryogenic pump (also known as a sorption pump), and a Boostivac system which is formed by the use of Titanium evaporation in conjunction with an Ultek ion pump.

The PVD apparatus is shown in Figure 2.4.
Figure 2.4 Physical vapor deposition apparatus. (1) Ion pump control section. (2) Boostivac control section. (3) Deposition control section. (4) LCD monitor. (5) Ion pump valve. (6) Sorption pump dewar. (7) Sorption pump. (8) Mechanical pump valve. (9) Mechanical pump gauge. (10) Deposition chamber.
2.3.2 Pumping Stage

An air-cooled mechanical pump is used in the rough pumping stage to create a vacuum of around 200 torr. Then the sorption pump operates to create higher vacuum by injecting liquid nitrogen rapidly into the sorption pump dewar (styrofoam bucket). The Boostivac system creates the lowest pressure to reach the deposition vacuum level.

2.3.3 Boostivac System

The Boostivac method of pumping operates on gases that can be chemically combined with titanium such as H\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2}. Titanium filaments in the system are heated to sublime titanium onto a substrate. The deposited titanium then combines with the gases, and permanently removes them from the system. Since titanium only combines with a specific group of gases, other means must be used to remove the remaining gases. The ion pump removes all gases but does not have the capacity to pump H\textsubscript{2}, O\textsubscript{2}, and N\textsubscript{2} as efficiently as the titanium film. When used together, they act to enhance each other; the ion pump ionizes gases such as H\textsubscript{2}O so that the byproducts interact with the titanium film and the titanium film provides high pumping speeds for gases most commonly known as residuals in vacuum systems\cite{43}.

Ion pump operation works as follows. A high magnetic field is used to contain and guide electrons. A high voltage is applied to separate electrons from molecules/atoms to form plasma, which is trapped inside the anode assembly by the high magnetic field. When gases move into the anode assembly, they are struck by electrons, becoming ions when the electrons are kicked out of the gas molecules. The positive ions are forced by the high electric field out of the anode assembly towards the cathode plate, forming solids. Thus, the gas molecules are removed from the system volume, creating
a high vacuum. A diagram for ion pump operation is shown in Figure 2.5.

![Diagram of ion pump operation](image)

**Figure 2.5** Ion pump operation: gas molecules such as $\text{H}_2$ (red), $\text{O}_2$ (blue), $\text{N}_2$ (yellow), are struck by fast moving electrons (black), becoming ions when the electrons (black) are knocked out of the gas molecules. The positive ions are forced by the high electric field out of the anode assembly to move towards the cathode plate, forming solids (gray), to remove gases from the system.

Operating controls for the Boostivac Ion Pump Control Unit are located on the front panel of the control tower. The top section of the front panel is for Ion Pump Control, and the Boostivac section is below it.

### 2.3.4 Operation

In general, the PVD process consists of three stages:

- Sorption pump baking, which usually takes 2 hours;
- Vacuum pumping, which usually takes 1.5 hours to reach the required vacuum level;
Material deposition, which takes a few minutes.

The bell jar should be maintained in vacuum below 200 torr even when the apparatus is not in operation. Below are the details of PVD operation:

1. The sorption pump is baked for 2 hours. To do so, first, the valve linking the sorption pump and the bell jar is turned off and the cork from the sorption pump is removed. Then, the sorption pump heater is placed on the enclosure and heater switch 1 on the control tower is turned on.

2. The deposition material is fed into the system by opening the mechanical pump valve to restore the bell jar to room pressure, then twisting open the bell jar and gently lifting it up. Removing the used tungsten boat from the holder and replacing it with a pre-cleaned new one, the appropriate amount of hydrochloride cleaned coating material (aluminum or silver) is placed inside the trough of the tungsten boat. The three mounting plates which hold the pre-cleaned glass substrates are placed on top to cover the three apertures. The bell jar is then closed, the cooling air turned on, and the bell jar is pumped down to 200 torr using mechanical pump. Lastly, the valve and the pump are turned off.

3. The LCD deposition rate and thickness monitor from the rear of the control tower is turned on.

4. The cooling water in the Boostivac system is turned on to cool the substrate area onto which the titanium film is deposited for effective pumping of gases such as H₂.

5. The Ion Pump Section is turned on. The functions of the buttons on the ion pump control panel are as follows:
• START: it should only be used to start the ion pump since a current overload condition in the output circuit will not trip the output circuit breaker in this mode.

• RUN: it should be used during the operation. A current overload condition cannot exist for more than 2 minutes without tripping the output circuit breaker in this mode.

• EIGHT-POSITION ROTARY SWITCH: this switch is located towards the right of the panel, which selects the ranges of current, pressure or voltage displayed on the adjacent meter. The current output to the ion pump is displayed linearly on the meter if the switch is in any of the first six positions. The ion pump pressure is displayed on the meter on a logarithmic scale ranging from $10^{-5}$ to $10^{-9}$ Torr if the switch is in the TORR position. The voltage output to the ion pump is displayed linearly on the meter if the switch is in the 5 KV position. This switch should be in the TORR position during operation for easy monitoring.

6. On the Boostivac section, the FILAMENT POWER is switched on, and FILAMENT SELECTOR is set to “1”. This four-position rotary switch selects any one of the four titanium sublimation filaments provided in the filament holder. Only one filament is powered on at a time.

7. The CYCLE/CONTINUOUS switch is set to CONTINUOUS, and the filament current set to a value within 50-55 Amps (yellow zone on the meter). In CONTINUOUS mode, power is applied to the Boostivac filament continuously. In CYCLE mode, the Timer Option (CYCLE LENGTH rotary switch) automatically controls the duty cycle of that filament.

8. The CYCLE/CONTINUOUS switch is set to CYCLE, and the CYCLE LENGTH
is set to 2 minutes.

9. Heater 1 is turned off, and the heater enclosure is removed. The cork is then set. The sorption pump dewar is placed onto the system, and the sorption pump valve is opened. Liquid nitrogen is added to the dewar to cool down the sorption pump until the top Ion Pump gauge reads in the middle of the $10^{-7}$ torr region and the auxiliary meter (right below the Boostivac section, in logarithmic scale) goes under 6. Occasionally the Ion pump valve is turned on/off multiple times to let in gases from the deposition chamber, which speeds up the depletion of gases.

10. Once the deposition chamber reaches the required vacuum level mentioned above, the deposition process is started by pressing the black power button on the deposition control section. Deposition current range is set to 0-250A, and the current slowly increased to 200A by turning the big knob next to the current meter.

11. The deposition rate and thickness is carefully monitored on the LCD. Once the coating reaches the desired thickness, the deposition current is cut off by pressing the red power button and then the current knob is turned back to ZERO.

12. The control tower is turned off and the system cools down for a few minutes after which the coated plates are removed.

13. The bell jar chamber is closed and pump down to 200 torr. The mechanical pump valve is then closed and the pump turned off. The cooling water and air is then turned off after a few minutes.

Figure 2.6 shows images of a PVD coated dye-doped polymer fiber segment sample:
2.4 Device Assembly

2.4.1 Polish and Cut Fiber

Once the dye-doped polymer fiber is prepared and partially reflective coverslips are made, we assemble them into the designed photomechanical structure. The first step is always to prepare fiber segments of the desired length, which is shown in Figure 2.7:

The tools needed are a fiber collet, fiber polish disk, 3-color lapping paper, diamond edge cutter, tweezers, ruler, and microscope.

First we place a section of polymer fiber into the fiber collet and fasten it so that it is firm enough to hold the fiber but not to damage it. Next we place the fiber collet into the polish disk, and make sure the end face of the fiber collet matches that of the polish disk so that only 1mm of fiber extends beyond the desired. The polish disk is
Figure 2.7 (a) Tools used in making a photomechanical dye-doped fiber include (b) a diamond fiber cutter, (c) a fiber collet that holds the fiber. The collet is placed in a polishing disk to polish. (d) A fiber in the collet extended to the cutting length, and (e) shown from a side view. (f) A cut fiber viewed under a microscope for length determination.
held perpendicular to the lapping paper surface and the fiber is gently polished using
a figure-eight motion starting with coarse grit of 3µm and ending with fine grit of
0.3µm. Once the degree of polish is optically smooth, compressed air is sprayed on
the fiber end to remove dust. Finally, the polished surface is inspected for quality
under a microscope or a fiber-endoscope. If a scratch is found, the polish process is
repeated until a scratch-free surface results.

Next, to make the desired length, the fiber is pulled out of the collet to a length
that is slightly longer than the desired length and placed on the diamond edge cutter
under a microscope, and cleaved using a pair of tweezers to quickly break the fiber. If
cracks are found after inspecting the cut fiber section, the process is repeated. Once a
suitable fiber is found, the other end of the fiber is polished using the same procedure
as above.

A multi-layer face mask is used at all times to protect the researcher from inhaling
the toxic fiber dust. The face mask also prevents the researcher from accidentally
launching the precious fiber with a gentle gust of breath.

2.4.2 Photomechanical Fabry-Perot Interferometer

A Fabry-Perot interferometer is constructed using three polymer fiber segments of the
same length as rigid supports which are sandwiched between two partially reflective
mirrors as shown in Figure 2.9. In order to align the two coverslips parallel, a special
mounting stage is built as shown in Figure 2.8.

The top coverslip with fiber supports attached is held in place by a clamp made
of two microscope slides. The bottom piece is placed on top of an optical tilt mount
which is attached to a translation stage to allow fine vertical control. A HeNe laser
beam is expanded before directed into the mounting assembly. If the two coverslips
are aligned parallel, the interference pattern shown on the viewing screen will be a
If the vertical tilt or the horizontal tilt is actuated by a laser beam launched into the fiber along its axis, the Fabry-Perot fringes will shift. By counting the shifts (either manually or by means of an oscilloscope), the tiny length change of the fiber can be calculated. The obvious advantage of this structure is its capability of three beam actuation which gives it more degrees of freedom to deflect a beam. However, the initial requirement of parallel alignment of the coverslips requires a complex fabrication stage as shown in Figure 2.8. When only one fiber leg is illuminated with a 355nm laser beam, the device response is unmeasurable due to the stiffness of the other two fiber legs. To overcome the stiffness issue, two spring loaded joints are used to replace the two non-actuating fiber supports in Figure 2.1(b). The spring is made by winding \( \varnothing 120\mu m \) fine copper wire (made by California Fine Wire) around a thin needle of the same diameter as the photomechanical fiber. A short fiber segment is
Figure 2.9 (a) Photograph of 4 photomechanical fibers of equal length and (b) a sketch of the final device structure

Figure 2.10 Copper springs

inserted inside to ensure the spring remains perpendicular to the substrate during the mounting process. The spring-loaded support makes the spring constant smaller than that of the fiber, but is still too stiff, so it makes photomechanical deflection unmeasurable.

2.4.3 Photomechanical Tilt Mount with C Leg

A photomechanical tilt mount with two C-shaped supports and a single fiber actuator sandwiched between two coated microscope coverslips is a design that allows photomechanical deflection to be observed. Figure 2.11 shows the geometric dimensions of the layout. Two segments of 15mm long $\varnothing 120\mu$m fine copper wires are glued
Figure 2.11 Design schematics of tilt mount (mm). The copper wires, shown in yellow, are glued in the positions as shown between the two coverslips and the photomechanical fiber is glued to the left plate on the upper left corner 2mm from the edges.

to the coverslips as joints. Then the polymer fiber of the desired length is prepared using previous steps and then is attached perpendicular to the coverslip using light-non-absorbing adhesive as shown in Figure 2.12(b). The fiber-glass contact is dried for at least 24 hours to make the contact permanent. Next the other coverslip is gently flipped to bend the copper wires into place to make smooth C shape. An appropriate amount of adhesive is applied on top of the fiber taking care not to break the bottom connection. Several coverslips are used as weights on top of the top coverslip to hold it down so that it makes contact with the fiber. It takes 24 hours for the adhesive to completely dry. A finished photomechanical tilt mount on a holder is shown in Figure 2.12(d). A drawing of the final assembly is shown in Figure 2.12(e). All experiments in this dissertation use this tilt mount design.
Figure 2.12 Assembly process
Chapter 3

Experiment

3.1 Introduction

In this chapter, we discuss experimental setups constructed to investigate the photomechanical response of dye-doped polymer fibers in a device configuration. We first discuss a graphical method initially used to test the feasibility of the photomechanical device, then describe the experimental technique which produces the most accurate and quantitative results.

3.2 Graphical Method

To probe a physical event, we often acquire visual results from experiments. For the Fabry-Perot interferometer device, an interference pattern is expected, as discussed in Section 2.4.2. The two mirror surfaces of the Fabry-Perot device are initially set parallel to each other in the fabrication process, as shown in Figure 2.8. If one of the fiber supports is actuated by the pump beam, the mirror tilts and the parallel configuration is lost. Thus the interference pattern will become a series of semi-
periodically spaced dots. The spacing between dots and the angle of the dot sequence will vary with the length change of the fiber.

Figure 3.1 shows an early-stage experimental setup to record the interference pattern using two screens. Two digital cameras are configured to record videos of the entire process and also to take a picture of the screen patterns automatically every 1 minute using computer control software. Due to the complexity of fabrication of these interferometers and difficulty in maintaining ultra-precise tolerances, an initially well aligned Fabry-Perot device seldom works. In these cases, the initial interference patterns are of the equal inclination type instead of Fabry-Perot’s concentric ring type.

![Figure 3.1 Setup for graphical method](image-url)
Figure 3.2 Time lapse video of beam deflection on screen 1. Frames are sequenced from left to right, and top to bottom.
A typical video contains more than 900,000 frames. Frames are extracted per 300, 1800, and 18000 frames by MATLAB script. Figure 3.2 shows 16 equally spaced frames of footage recorded on screen 1: from frame 18000 to frame 720000. By carefully comparing each subsequent frame, we found the interference pattern rotated slightly counterclockwise when pump laser is on, which indicates the fiber undergoes a change in its physical dimensions. Figure 3.3 shows the photo of the original Fabry-Perot device.

Figure 3.3 Original Fabry-Perot device

3.3 Main Experiment

3.3.1 Introduction

In order to acquire accurate displacement information, a PSD (position sensitive device) is used. The position sensitive device used in the experiment is a Phreshphotonics SiQu50-TIA quadrant photodiode which consists of four distinct photosensitive elements separated by a 100µm gap. When a light spot illuminates one element, only that element will produce photocurrent; when the light spot translates across the sur-
face of the detector, the energy becomes distributed between adjacent elements. The photocurrent is converted into a voltage signal through a high performance current-to-voltage amplifier. The differential output signal gives the position of the beam spot. However, the quadrant detector can only provide position information when the beam spot is in the vicinity of the center and thus overlapping with all four quadrants. If the beam spot moves completely onto one side with the detector center outside of the beam spot, the output of the detector will not provide relative position information of the beam spot. The same is also true when the beam spot falls into a single quadrant. To ensure illumination of all four quadrants, the probe beam is expanded or defocused before entering the sample stage.

![Quadrant photodiode](image)

**Figure 3.4 Quadrant photodiode**

The quadrant photodiode output is converted into X and Y position using,

\[
X = \frac{(A_1 + A_4) - (A_2 + A_3)}{Sum},
\]

(3.1)

\[
Y = \frac{(A_1 + A_2) - (A_3 + A_4)}{Sum},
\]

(3.2)

where \(A_1, A_2, A_3, A_4\) are the voltage outputs of each quadrant, and \(Sum = A_1 + A_2 + A_3 + A_4\).

For simplicity, we can drop the denominators of the above equations, and only use the numerators to represent the X and Y positions, which we will later see is valid.
### 3.3.2 Calibration of Quadrant Photodetector

Figure 3.5 Quadrant photodiode voltage output vs beam spot location.

Figure 3.5 shows the relation between position information of beam spot on the quadrant detector and its voltage output. During the calibration process, a X-Y translational stage is used to generate the displacement of the beam spot across
quadrants. When calibrating one direction, the other is kept fixed. It can be verified that the voltage outputs of the two orthogonal directions are independent of each other as shown in Appendix B. The minimum increment of the micrometer used along the X direction is 10µm while that along the Y direction is 25.4µm. The incident laser power at 633nm before entering the quadrant detector is 1.37mW. As shown in Figure 3.5(a) and Figure 3.5(b), if the beam spot displacement is in the vicinity of the origin, the relation along both X and Y directions can be described by a linear function. If further away, a polynomial fit function must be used. In the experimental investigations carried out, all measurement results fall in this linear region.

3.3.3 Experimental Setup

The photomechanical response of the dye-doped polymer fiber is acquired by measuring the deflection of a 633nm probe beam using a quadrant photodiode (Phresh Photonics SiQu50-TIA) in the experimental setup shown in Figure 3.6 and Figure 3.7. When a pump beam of 355nm (Coherent Innova 90K Krypton laser) is directed on-axis into the DR1-doped PMMA polymer fiber support of the photomechanical tilt mount, a length change is activated. The probe beam is deflected by a change in tilt angle of the upper mirror in response to the change in fiber length. Thus the expanded probe beam of 633nm is deflected away from the center of the quadrant detector, generating non-zero voltage outputs. The output signal is conditioned by a custom-designed amplifier circuit box which converts the direct outputs of the quadrant photodiode into a voltage range which the data acquisition device (DAQ) accepts. The DAQ device used is a LabJack U3-LV which can only accept 0-2.4V analog inputs, shown in Figure 3.8. A probe beam at 633nm and of 20mW power is directed to the top partially reflective surface of the photomechanical device through a non-polarizing beam splitter (BS). Then the reflected beam goes through the BS
again and enters the quadrant photodiode through an OG590 color glass filter which keeps the scattered pump beam from entering the detector. The probe beam must be expanded to make the quadrant detector produce meaningful position information. The 633nm laser beam on the other arm of the pump path is used for beam alignment and comparison. The two pump beams are combined through a dichroic mirror optimized at 355nm. Two Uniblitz laser shutters are used to provide modulation to the pump beams. Data acquisition and shutter control are synchronized by LabVIEW® virtual instrument software, which can also operate independently.

**Figure 3.6** Main experimental setup
Figure 3.7 Main experimental setup. Red and blue lines represent HeNe and Krypton laser beams. Components in yellow boxes from left to right: dichroic mirror, quadrant photodiode, OG590 color glass filter (above), beam expander (below), photomechanical device.

Figure 3.8 Supplemental circuits. Components in yellow boxes from left to right: LabJack U3-LV, signal conditioning circuit Box, DC power supply for Uniblitz shutters (bottom left), pull-up circuit for Uniblitz shutter (top right), DC tri-power supply for quadrant photodiode (bottom right).

Figure 3.9 is the close-up picture of the photomechanical tilt mount mounted on a glass slide platform. Figure 3.10 shows a typical quadrant photodiode operation
when a 355nm pump laser beam is turned on at 300s over a 600s measurement. When the shutter is closed, $X$ and $Y$ remain constant at ZERO volts. When the shutter is open at 300s, $X$ and $Y$ respond instantaneously to the UV irradiation. We notice that $\text{Sum}$ undergoes a slight voltage increase which will be explained later. The $Y$ response is much larger than $X$, which is due to the design geometry of this particular photomechanical device. Over the entire span of the measurement, $\text{Sum}$ remains constant except during the turn-on period. The absolute change of $\text{Sum}$ upon turn-on is much smaller than those of $X$ and $Y$, where $\text{Sum}$ is much larger than either $X$ or $Y$. We thus drop the $\text{Sum}$ term in Equation 3.2 and use the absolute values of $X$ and $Y$ voltages to represent the photomechanical response. Figure 3.11 shows another typical quadrant photodiode operation mode when the pump beam is modulated by a shutter or a chopper wheel.
Figure 3.10 Typical quadrant photodiode response to a step pump intensity.

Figure 3.11 Modulated outputs of X and Y to a modulated intensity.

The quadrant photodiode is made of four segmented units which are separated
by small gaps. When a laser beam illuminates the detector in the center, not all of the energy generates photocurrent. Those photons striking the gap region will not produce current. So the effective detection area is the beam spot area minus the gap area enclosed by the beam spot. The gap area reaches its maximum when the beam spot is in the center of the detector, which is shown in Figure 3.12. If the beam spot moves away from the center, the gap area enclosed by the beam will decrease, resulting in an effective detection area that increases, which increases the $Sum$ voltage output.

![Figure 3.12 Beam deflection on quadrant photodiode](image)

3.3.4 Vibration

Mechanical vibration is always a concern in most experiments that involve precise beam alignment. To minimize its influence, rubber cushions are used to mount Uniblitz shutters to the table. All of the optics and lasers are mounted on sturdy optical holders. A control experiment with the same ambient conditions but UV pump beam blocked confirms that the three detector outputs, i.e., $Sum$, $X$, $Y$, give constant readings at ZERO, which rules out shutter vibration as the cause of the abrupt beam deflection in the step pumping case.
3.4 Supplemental Experiment

Aside from the main experiment, a supplemental experiment aimed to measure the influence of photoreorientation is constructed on the other side of the same optical table shown in Figure 3.13. The pump-probe setup consists of the same gas laser operating at 355nm and a diode laser at 636nm. The Coherent Innova 90K Krypton laser emits UV light centered at 355nm which passes through a short pass filter(UG-11) to remove longer wavelengths. The pump beam is chopped at 100Hz and combined with the probe beam by a dichroic mirror optimized at 355nm. The probe beam power is monitored by a precision powermeter at 0.613mW. The two beams are coupled into the 1cm long fiber sample, and sent to a long pass filter(OG-590) afterwards to remove the unwanted UV pump light. The vertical and horizontal polarization components of the transmitted probe beam are separated by a polarized beam splitter. Photodiode 2(PD2) detects pure horizontal polarization. The vertical polarization is picked up by photodiode 1 (PD1). Data acquisition is through a LeCroy 9360 dual channel oscilloscope and retrieved through LabVIEW®. This experiment is used to measure the degree of dichroism induced by the pump beam, which is associated with molecular reorientation, a mechanism that can lead to photomechanical deformation.
Figure 3.13 Experimental setup for photoreorientation measurement
Chapter 4

Results and Discussions

4.1 Experimental Results

The photomechanical response is obtained using a pump-probe experimental setup shown in Figure 3.6. It converts a photomechanical length change of the fiber into a deflection of the reflected probe beam. Figure 4.1 shows the schematic diagrams of the way the length change is determined from beam deflection. This view represents the Y response in the results. The dashed beam path designates the zero position on the quadrant photodiode. If the fiber support elongates, the beam center moves towards the negative quadrants; if the fiber support contracts, the beam center moves towards the positive quadrants.

A timed measurement is carried out when the pump beam is turned on and off by an UNIBLITZ laser shutter. The modulated response is shown in Figure 4.2. The deflections in X and Y are represented by the voltage outputs of the quadrant photodetector along the vertical and horizontal direction. (By Y deflection, we mean the deflection which is associated with the tilt of top coverslip in the section view plane shown in Figure 4.1 and causes the probe beam to move along the vertical Y
direction on the quadrant detector; By X deflection, we mean the deflection which is associated with the tilt perpendicular to the section view plane and causes the probe beam to move along the horizontal X direction on the quadrant detector). Within the measurement range, the voltage outputs of the photodetector are linearly proportional to the displacement of the beam spot in both directions. When the deflection is small, this displacement is also proportional to the length change of the fiber in the small angle approximation. Thus, for simplicity, we will use the voltage output to represent the length change. As shown in the timed measurement, the fiber length changes with the pump beam on and almost relaxes to its original length with the pump turned off. The fact that the vertical(red) direction response is a bit different than the horizontal(black) direction is due to the asymmetrical design geometry of the deflection measurement apparatus as shown in Figure 2.1(c).
Figure 4.2 Photomechanical response as a function of time when the pump beam is turned on and off.

Figure 4.3 System drifts

A careful examination of the exact magnitude of the X and Y deflections reveals
that the fiber is not fully restored during each cycle. This is mainly due to the
restoring efficiency of the material, shutter vibration and system drift. The restoring
efficiency represents the percentage of the molecules which can fully restore to their
original state when the photo stimulus is withdrawn.

Though care has been taken to minimize the influence of mechanical vibration of
the laser shutter, it still shows non-zero contribution to the total noise. We also ob-
serve system drift which is always linear with time. Figure 4.3 shows the background
drift with all the pump laser and shutters powered off over nearly two hours of run
at night.

The responses from three voltage outputs are linear fitted with relation \( y = kx + b \).
The fitting parameters are given in Table 4.1:

\[
\begin{array}{ccc}
  k & b \\
  Sum & 2.52682E-6 \pm 5.15028E-9V & 2.85122 \pm 1.94866E-4V \\
  X & -7.45788E-5 \pm 2.02198E-8V & -0.03833 \pm 7.65038E-4V \\
  Y & 4.96319E-5 \pm 1.29164E-8V & -0.00619 \pm 4.88706E-4V \\
\end{array}
\]

Table 4.1 Parameters of fitting functions for Figure 4.3

The slope for each fitted line represents the drifting rate, and for \( Sum, X, Y \), they
are \( 2.5\mu V/s, -74.6\mu V/s, 49.6\mu V/s \). Then the total drift for a typical experimental
measurement is as shown in Table 4.2:

\[
\begin{array}{cccccc}
  \text{Nominal Value} & \text{Drift Rate} & \text{600s Drift} & \text{Drift Ratio} & \text{20s Drift} & \text{Drift Ratio} \\
  Sum & 3V & 2.5\mu V/s & 1.5mV & 0.05\% & 0.050mV & 0.00167\% \\
  X & 2V & -74.6\mu V/s & -44.76mV & 2.24\% & -1.492mV & 0.0746\% \\
  Y & -1.5V & 49.6\mu V/s & 29.76mV & 2\% & 0.992mV & 0.066\% \\
\end{array}
\]

Table 4.2 System drifts ratio
As shown in Table 4.2, the system drift is so small that it can be safely omitted in data analysis. Another factor that needs to be taken into consideration is the noise introduced by shutter operation, which is shown in Figure 4.4. The shutter is opened at 10s, which causes a jump in both X and Y, estimated as 0.5mV for both using the Savitzky-Golay smoothing method shown as solid curves. The analysis uses Origin Pro®. Compared with nominal values of X and Y, the effect of the shutter operation noise can also be neglected.

![Figure 4.4 Shutter operation noise.](image)

To further understand the dynamics, a single shot measurement is carried out. Figure 4.5 shows the response when the UV pump beam is turned on at 10s, which induces a length change of the fiber support. The typical length change of the 475µm thick, 5mm long fiber is calculated to be 5µm for 10mW power of incident UV light. Both X and Y direction deflections show two distinct rates of change: a fast and a slow processes. By fitting each direction with a double exponential decay function,
time constants for both fast and slow processes are determined. The fitting function is given by

\[ X \text{ or } Y = A_0 + A_1 \exp \left( -\frac{t - t_0}{t_1} \right) + A_2 \exp \left( -\frac{t - t_0}{t_2} \right), \]  

(4.1)

and the fitting parameters are shown in Table 4.3.

![Figure 4.5](image)

**Figure 4.5** Photomechanical response as a function of time after the UV pump beam is turned on.

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_0 )</td>
<td>0.467 ± 0.023V</td>
<td>-1.041 ± 0.005V</td>
</tr>
<tr>
<td>( t_0 )</td>
<td>10.000 ± 0.005s</td>
<td>10.000 ± 0.005s</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>-0.770 ± 0.017V</td>
<td>0.577 ± 0.013V</td>
</tr>
<tr>
<td>( t_1 )</td>
<td>0.133 ± 0.005s</td>
<td>0.157 ± 0.007s</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>0.155 ± 0.020V</td>
<td>0.533 ± 0.004V</td>
</tr>
<tr>
<td>( t_2 )</td>
<td>8.416 ± 2.253s</td>
<td>4.220 ± 0.128s</td>
</tr>
</tbody>
</table>

**Table 4.3** Parameters of fitting functions for Figure 4.5
Figure 4.6 Measured intensity dependence of the time constants for Y deflection
Figure 4.7 Measured intensity dependence of the time constants for X deflection
Time constants for both fast processes stay comparable, i.e., 0.133s for X, and 0.157s for Y, which indicates they may be caused by the same mechanism. Figure 4.6 and Figure 4.7 show an intensity dependence measurement. To vary the intensity of the UV pump laser beam, a set of Thorlabs neutral density (ND) filters are used since plain cubic polarizers absorb UV light strongly. The ND filter characteristic absorbance of the UV pump wavelength is calibrated against a photodiode with a linear operation region between 350-1000nm. The incident laser power is maintained at 10mW.

![Graph](image)

**Figure 4.8** Example of measured mirror reflection while force is applied to the reflector with pump beam off.

A sharp eye may find X and Y in Figure 4.5 show two different trends: Y is monotonically decreasing while X declines after the sharp transient. Since X and Y both should reflect the same physical property of the fiber support while changing length, one would expect they must show the same trend as does the example shown in Figure 4.8. These data are taken while mechanically applying a force to the platform.
which holds the tilt mount with pump beam off.

Thus the decreases of X after the initial rise must originate in the strained reflection from the top coverslip which is supported by the fiber and Copper wires. When the fiber changes its length upon light irradiation, the asymmetrically designed C spring leads to a different deflection along both the X and Y directions if the C springs are not properly attached to the coverslip. System drift may also be relevant but is not observed in the Y direction, so is probably the cause. Another factor could be material fatigue which can enhance this asymmetry.

To overcome the above issue, care has been taken to minimize surface strain of the top coverslip glass (and drift) and improve the signal to noise ratio of the detectors, which results in cleaner response curves shown in Figure 4.9.

![Figure 4.9](image-url)  

**Figure 4.9** Photomechanical response as a function of time in response to a linearly polarized pump beam turned on at 10s and off at 15.5s with polarization perpendicular to the optical table. (Black data set from 0-20s) deflection in X direction, (red smooth curve from 10-15.5s) best fitting for X, (red data set from 0-20s) deflection in Y direction, (blue smooth curve from 10-15.5s) best fitting for Y.
Fitting parameters using Equation 4.1 are given in Table 4.4. The fitting functions are plotted as smooth solid curves.

<table>
<thead>
<tr>
<th></th>
<th>X</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_0$</td>
<td>1.901±0.002V</td>
<td>-1.643±0.016V</td>
</tr>
<tr>
<td>$t_0$</td>
<td>10±0.005s</td>
<td>10±0.005s</td>
</tr>
<tr>
<td>$A_1$</td>
<td>-0.715±0.216V</td>
<td>0.650±0.017V</td>
</tr>
<tr>
<td>$t_1$</td>
<td>0.058±0.015s</td>
<td>0.180±0.010s</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-1.122±0.225V</td>
<td>0.890±0.009V</td>
</tr>
<tr>
<td>$t_2$</td>
<td>0.181±0.019s</td>
<td>2.878±0.137s</td>
</tr>
</tbody>
</table>

Table 4.4 Parameters obtained by fitting the functions in Equation 4.1 to the data in Figure 4.9

Time constants for both fast processes are $t_{x1} = 0.058±0.015s$ and $t_{y1} = 0.180±0.010s$. The bump in the Sum output of the quadrant detector in the top left inset of Figure 4.9 is caused by the gap between adjacent quadrants (100µm for Phresh Photonics SiQu50-TIA QPD). The gap area enclosed by the beam spot is maximized when the beam is at the origin of the four quadrants. Thus the effective total detection area of the QPD is at minimal when the probe beam is illuminating the QPD center spot. To reduce the gap effect, a properly expanded probe beam is needed.

We believe that this photomechanical effect observed in the experiment could originate in both macroscopic and molecular processes. The physical processes include thermal expansion of the substrate PMMA polymer matrix and photoreorientation of the DR1 dye molecules. The molecular process originates in isomerization between trans- and cis- DR1 isomers, which consists of three types: trans-cis photoisomerization, cis-trans photoisomerization, and cis-trans thermal isomerization. The dye molecules undergo a conformational change which induces a strain that deforms the
polymer.

Photoisomerization is reported to be on the 10ns time scale in liquid crystals by transient absorption spectroscopy[44]. Changes in the re-orientational order is a diffusion process which acts over a much longer time scale[45]. Photothermal heating, which also results in a length change of the fiber support, is a slower process. The direct measurement of the photoisomerization process requires rather complex spectroscopic techniques[46], but photoreorientation can be measured using optical techniques as described in our paper[1].
4.2 Photoreorientation

When linearly polarized light interacts with an azobenzene-group containing polymer material, dye molecules in the ground state are excited depending on the orientation of molecules with respect to the polarization of the light. After several excitation-relaxation cycles, the excited molecules must come back to a ground state in an orientation that minimizes the probability of excitation, so molecules accumulate in the direction perpendicular to the light’s polarization. Thus, dye molecules initially aligned parallel to the polarization tend to move away from that direction, and re-orient to the perpendicular direction. More specifically, only those chromophores with a component of the transition dipole moment parallel to the light polarization are preferentially activated[25]. There are two such directions: one is the light propagation direction, and the other is the direction perpendicular to the meridian plane. The change of chromophore population in the latter can be measured optically.

The measurement setup of this supplemental experiment is shown previously in Figure 3.13. The pump beam is linearly polarized and in order to maintain its linear polarization through multiple reflections, the polarization is kept vertical[47, 48](perpendicular to the optical table). The probe beam is either vertical or horizontal. The strong pump beam will re-orient the UV sensitive dye molecules. Thus the probe beam detects a changing population of the dye molecules in the vertical and horizontal directions. The photodiodes after the UV block filter will detect a changing ratio between the two polarization components of the probe beam as the orientational distribution function changes.

In theory, a linearly polarized light should remain in its polarization when it travels through a fiber because there should be no conversion between the two polarization components. In practice, linearly polarized light at the fiber input is generally
transformed into elliptically polarized light at the fiber output caused by the random power transfer between the two polarizations, which is the result of slight random imperfections and uncontrollable strains in the fiber[49].

Figure 4.10(a) shows the measurement results of the configuration where both the pump and probe beam polarizations are perpendicular to the optical table. When the 355nm pump light is turned on, the outputs of the two polarization components picked up by photodetector 1 and 2 immediately follow the pump’s oscillation. Since the chopped pump beam is blocked out by the long pass filter (LPF), the oscillation of the outputs shows a strong optical switching effect, a light controlled intensity change. Within each oscillation period, the ratio of the two polarization components remains almost constant within detectable intensity range.

Figure 4.10(b) shows the measurement results of the configuration that the pump beam polarization is perpendicular but with the probe beam polarization parallel to the optical table. The ratio of the two polarization components also remains constant within each oscillation period.

Circularly polarized laser light is considered not to induce photoreorientation where coherent illumination is needed since circular polarization activates dye molecules in all directions and on average leads to no preferential direction for the dye molecule population to accumulate. A comparison experiment is carried out using circularly polarized pump beam by inserting a quarter waveplate (at 355nm) in the beam path between the UV mirror and the chopper. After the reflection by the dichroic mirror, an extra phase shift is added to the UV beam which makes it slightly elliptical[47, 48]. Figure 4.11(a) and Figure 4.11(b) show the measurement results for the two corresponding cases as in linear polarization measurements. They do not show evidence of photoreorientation.

The supplemental experiment shows that linear polarization measurement results
Figure 4.10 Probe light transmitted through a fiber pumped with UV light as a function of time.
Figure 4.11 Probe light transmitted through a fiber pumped with UV light as a function of time.
are comparable to the circular polarization cases, which implies a very weak presence of photoreorientation in the fiber.

![Graph showing photomechanical response](image)

**Figure 4.12** Photomechanical response as a function of time in response to a circularly polarized pump beam turned on at 10s and off at 15.5s with polarization perpendicular to the optical table. (Black data set from 0-20s) deflection in X direction, (red smooth curve from 10-15.5s) best fitting for X, (red data set from 0-20s) deflection in Y direction, (blue smooth curve from 10-15.5s) best fitting for Y.

In order to further rule out the influence of photoreorientation, a circularly polarized pump beam is employed in the main experiment (Figure 3.6) by inserting the quarter waveplate between the dichroic mirror and the prism. The photomechanical response is shown in Figure 4.12. Fitting parameters using Equation 4.1 are given in Table 4.5. The signal to noise ratio in the circular polarization measurement is lower than that in the linear case, which is caused by the imperfections in the quarter waveplate. Time constants for fast processes are $t_{x1} = 0.057 \pm 0.023s$, and $t_{y1} = 0.142 \pm 0.016s$, which is in agreement with the linearly polarized measurement.
Table 4.5 Parameters of fitting functions for Figure 4.12.

The experimental results show no evidence of photoreorientation and its contribution to the length change of the fiber, only leaving isomerization and photothermal heating as the probable mechanisms.
4.3 Photoisomerization

Under visible irradiation, azobenzene-group-containing compounds can undergo cis to trans isomerization which tends to result in elongation, as shown in Bian’s previous experiment[21]; otherwise, if under ultraviolet irradiation, trans to cis isomerization should result in contraction. The experimental results in Figure 4.9 show elongation as the fast process, which indicates the competing cis to trans isomerization mechanism takes the dominant role in this process.

Photoisomerization involves both photochemical and thermal processes. The photochemical process consists of the trans-cis isomerization under UV irradiation and the cis-trans isomerization under visible irradiation. Since the cis isomer is unstable, it can undergo thermal back relaxation to the trans form. The composition of the two isomers changes with time, approaching asymptotically to a stationary state determined by the illumination wavelength[32]. At the photostationary state, the photochemical trans-cis rate must be equal to the photochemical cis-trans rate plus the thermal cis-trans rate[31]. Thus the dynamic rate equation for the trans and cis isomers is given by[25]

\[
\frac{\partial n_t}{\partial t} = -\Phi_{tc} P_t n_t + \Phi_{ct} P_c n_c + \gamma n_c \tag{4.2}
\]

and

\[
n_t + n_c = N, \tag{4.3}
\]

where \(n_t(n_c)\) is the number density of trans(cis) molecules, \(N\) is the total number density of chromophores, \(P_t(P_c)\) is the probability of absorption of a photon by a trans(cis) molecule; \(\Phi_{tc}(\Phi_{ct})\) is the quantum yield of the photochemical trans-cis(cis-trans) isomerization, and \(\gamma\) is the rate constant of thermal cis-trans back relaxation. And \(P_t(P_c)\) is given by

\[
P_j(\theta) = I_{pump} \sigma_j [1 + 2e_j e P_2(\cos \theta)] \tag{4.4}
\]
where $\theta$ is the angle between the direction of the trans molecule and the polarization of the pump beam. $\bar{\sigma}_j$ is the average absorption cross section and $e_j$ is the molecular anisotropy, of trans ($j = t$) and cis ($j = c$). And $\bar{\sigma}_j = (\sigma_\parallel + 2\sigma_\perp)/3$, $e_j = (\sigma_\parallel - \sigma_\perp)/(\sigma_\parallel + 2\sigma_\perp)$. $P_2$ is the Legendre polynomial

$$P_2 = \frac{1}{2} (3 \cos^2 \theta - 1)$$

$\epsilon = 1$ for linear polarization and $\epsilon = -\frac{1}{2}$ for circular polarization\[26\]. For linearly polarized light,

$$P_j(\theta) = I_{\text{pump}}[\sigma_\perp + (\sigma_\parallel - \sigma_\perp) \cos^2 \theta] \quad (4.5)$$

and, for circularly polarized light,

$$P_j(\theta) = I_{\text{pump}}[\sigma_\perp + \frac{1}{2}(\sigma_\parallel - \sigma_\perp) \sin^2 \theta] \quad (4.6)$$

Fischer et al.\[30\] observed that photoisomerization equilibrium is wavelength dependent, and the concentration of the cis isomer is maximized for 365nm wavelength irradiation. Zimmerman\[31\] showed that the quantum yields for both trans and cis photochemical isomerization depend only on wavelength of irradiation, and are approximately constant over a single absorption band at a given temperature. Typical values of average quantum yields for the UV band are cis-trans 0.42±0.04, trans-cis 0.11±0.01; for visible, cis-trans 0.48±0.05, trans-cis 0.24±0.02. Later Fischer\[32\] reported the quantum yields of photoisomerization strongly depend on temperature, and that the photoequilibrium shifts towards the trans isomer with cooling, provided that thermal isomerization is absent.

In our experiment, the UV pump laser power is stabilized at 10mW before entering the 475$\mu$m diameter fiber. With significant amount of heat transferring into the fiber, the internal temperature rises quickly, which drives up the rate of thermal isomerization and increases the trans isomer population. Meanwhile, the photoisomerization equilibrium shifts towards the cis isomer. If we assume the initial number
density of both trans and cis isomers are equal, with the second term on the right hand side of Equation 4.2 decreasing and the first term going more negative, the third term should be large enough to overcome the loss of trans population to keep $\partial n_t/\partial t$ positive, which indicates thermal cis-trans isomerization takes the dominant role in the fast elongation process.

Thus in order to recover contraction under UV irradiation, thermal heating effect must be reduced. A first thought is to reduce the incident laser power. While the laser power is kept at 10mW, a set of Thorlabs ND filters are used to change the incident power entering the fiber. For experiments with ND filters of which optical density varies from 0.1 to 1.5, all results show elongation in the fast process. To understand it, one would view this as follows. The ratio between rate constants for both directions, i.e., $(\Phi_{ct}P_c + \gamma)/\Phi_{tc}P_t$, is independent of intensity or weakly depends on intensity over the intensity range tested. If the balance of competition between trans-cis and cis-trans isomerization can be tuned, a contraction may be feasible.
4.4 Mechanical Constraints

The photomechanical tilt mount consists of various mechanical components which could also contribute to part of the total photomechanical response. A simplified mechanical model is shown in Figure 4.13. The parameters are as follows:

- $x, x'$: Length change of fiber and C spring from equilibrium position
- $x_g$: Displacement of center of mass of top coverslip from equilibrium position
- $x_0$: Equilibrium position of the system center of mass
- $L_1, L_2$: Axial distance of springs from center of mass of top coverlip
- $F_1, F_2, G$: Spring forces of fiber, C spring and force of Gravity
- $\theta$: Angular displacement of the top coverslip
- $k_1, c_1$: Spring constant and damping coefficient of the fiber
- $k_{2x}, k_{2y}$: Spring constants of C spring along X and Y directions

Figure 4.13 Section view of mechanical model
Figure 4.14 shows how $k_2$ is defined.

![Diagram](image)

**Figure 4.14** Displacement of C spring has effective spring constant of $k_2$.

### 4.4.1 Equations of Motion

Choosing the center of mass of the top coverslip as the pivot point, the equations of motion can be written as

$$
(k_1 x + c_1 \dot{x}) + (k_2 x' + c_2 \dot{x'}) = -m \ddot{x}_g,
$$

(4.8)

and

$$(k_1 x + c_1 \dot{x})L_1 - (k_2 x' + c_2 \dot{x'})L_2 = -J \ddot{\theta},
$$

(4.9)

with

$$
x_g = x - L_1 \theta,
$$

(4.11)

and

$$x' = x - (L_1 + L_2) \theta.
$$

(4.12)

Substituting Equation 4.11 and 4.12 into Equation 4.8 and 4.9, we get,

$$
k_1 x + c_1 \dot{x} + k_2 [x - (L_1 + L_2) \theta] + c_2 [x - (L_1 + L_2) \theta] = -m (x - L_1 \theta),
$$

and

$$(k_1 x + c_1 \dot{x})L_1 - \left\{k_2 [x - (L_1 + L_2) \theta] + c_2 [x - (L_1 + L_2) \theta]\right\} L_2 = -J \ddot{\theta}.
$$
Regrouping terms by \(x\) and \(\theta\) results in,

\[
m\ddot{x} + (c_1 + c_2)\dot{x} + (k_1 + k_2)x = mL_1\ddot{\theta} + c_2(L_1 + L_2)\dot{\theta} + k_2(L_1 + L_2)\theta, \quad (4.13)
\]

and \((c_2 L_2 - c_1 L_1)\dot{x} + (k_2 L_2 - k_1 L_1)x = J\ddot{\theta} + c_2 L_2(L_1 + L_2)\dot{\theta} + k_2 L_2(L_1 + L_2)\theta. \quad (4.14)\]

There are six variables \(\{\ddot{x}, \dot{x}, x; \ddot{\theta}, \dot{\theta}, \theta\}\) and only two equations. To be able to solve the problem, either a third independent relation needs to be found or at least one variable needs to be eliminated. The second approach is readily applicable.

If \(c_1 = c_2 = 0\), the above equations reduce to the damping-free form,

\[
m\ddot{x} + (k_1 + k_2)x = mL_1\ddot{\theta} + k_2(L_1 + L_2)\theta,
\]

and \((k_2 L_2 - k_1 L_1)x = J\ddot{\theta} + k_2 L_2(L_1 + L_2)\theta. \quad (4.15)\]

Regrouping terms by \(\ddot{\theta}\) and \(\dot{x}\), then

\[
\ddot{\theta} + \frac{k_2(L_1 + L_2)}{mL_1}\theta = \frac{1}{L_1}\ddot{x} + \frac{k_1 + k_2}{mL_1}x, \quad (4.15)
\]

and \(\ddot{\theta} + \frac{k_2(L_1 + L_2)}{J}L_2\theta = \frac{1}{J}(k_2 L_2 - k_1 L_1)x. \quad (4.16)\]

Solving for \(\theta\) and \(\ddot{\theta}\) in terms of \(x\) and \(\ddot{x}\),

\[
\theta = \frac{J m\ddot{x} + [k_1(J + mL_1^2) + k_2(J - mL_1 L_2)]x}{k_2(L_1 + L_2)(J - mL_1 L_2)}, \quad (4.17)
\]

and \(\ddot{\theta} = -\frac{m L_2 \dddot{x} + k_1(L_1 + L_2)x}{J - mL_1 L_2}. \quad (4.18)\]

If \(L_1 = L_2 = l\) and assume the top coverslip is uniform, then

\[
J = \frac{1}{3}(L_1^3 + L_2^3) \rho
\]

\[
= \frac{1}{3}(L_1^3 + L_2^3) \frac{m}{L_1 + L_2}
\]

\[
= \frac{2}{3} \frac{ml^3}{2l} = \frac{1}{3} ml^2.
\]
Substituting $J$ into $\theta, \ddot{\theta}$, we get

$$\theta = -\frac{m}{4k_2 l} \left( \ddot{x} + \frac{4k_1 - 2k_2}{m} x \right),$$

(4.19)

and

$$\ddot{\theta} = \frac{3}{2l} \left( \ddot{x} + \frac{2k_1}{m} x \right).$$

(4.20)

The results for a more general case with only $c_2 = 0$ can also be written as,

$$\theta = \frac{Jm \ddot{x} + (J + mL_1^2)c_1 \dot{x} + [k_1(J + mL_1^2) + k_2(J - mL_1L_2)]x}{k_2(L_1 + L_2)(J - mL_1L_2)},$$

(4.21)

and

$$\ddot{\theta} = -\frac{mL_2 \ddot{x} + (L_1 + L_2)c_1 \dot{x} + k_1(L_1 + L_2)x}{J - mL_1L_2}.$$

(4.22)

With $J = \frac{1}{3} ml^2$,

$$\theta = -\frac{m}{4k_2 l} \left( \ddot{x} + \frac{4c_1}{m} \dot{x} + \frac{4k_1 - 2k_2}{m} x \right),$$

and

$$\ddot{\theta} = \frac{3}{2l} \left( \ddot{x} + \frac{2c_1}{m} \dot{x} + \frac{2k_1}{m} x \right).$$

The first equation can also be written as,

$$2l\theta = x - \frac{m\ddot{x} + 4c_1 \dot{x} + 4k_1 x}{\frac{2k_2}{\text{Mechanical}}}. $$

(4.23)

The LHS of Equation 4.23 represents the nominal photomechanical response which is directly detected by the experiment. The first term on the RHS of Equation 4.23 is the direct photomechanical contribution from the fiber, and the second term is the contribution from the mechanical cell. Due to the asymmetrical design of the mechanical cell, $k_2$ is split into two, with $k_{2x}$ representing the spring constants in X direction and $k_{2y}$ in Y direction. Thus Equation 4.23 can be written as,

$$2l\theta = x - \frac{m\ddot{x} + 4c_1 \dot{x} + 4k_1 x}{\frac{2k_{2x}}{k_{2x}}}.$$ 

(4.24)

and

$$2l\theta = x - \frac{m\ddot{x} + 4c_1 \dot{x} + 4k_1 x}{\frac{2k_{2y}}{k_{2y}}}. $$

(4.25)

The fact that $k_{2x} \gg k_{2y}$ results that the motion in Y direction is more constrained, leading to a much longer time constant in the slow process. It also makes the second
term on the RHS of Equation 4.24 smaller than that of Equation 4.25, which results in a larger response in X direction than in Y direction.

<table>
<thead>
<tr>
<th></th>
<th>$X_{\text{lin}}$</th>
<th>$Y_{\text{lin}}$</th>
<th>$X_{\text{circ}}$</th>
<th>$Y_{\text{circ}}$</th>
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<tbody>
<tr>
<td>$A_0(V)$</td>
<td>1.901± 0.002</td>
<td>-1.710± 0.033</td>
<td>1.268± 0.003</td>
<td>-1.116± 0.030</td>
</tr>
<tr>
<td>$t_0(s)$</td>
<td>10± 0.005</td>
<td>10± 0.005</td>
<td>10± 0.005</td>
<td>10± 0.005</td>
</tr>
<tr>
<td>$A_1(V)$</td>
<td>-0.715± 0.216</td>
<td>0.296± 0.045</td>
<td>-0.093± 0.100</td>
<td>0.029± 0.086</td>
</tr>
<tr>
<td>$t_1(s)$</td>
<td>0.058± 0.015</td>
<td>0.058± 0.015</td>
<td>0.057± 0.023</td>
<td>0.056± 0.061</td>
</tr>
<tr>
<td>$A_2(V)$</td>
<td>-1.122± 0.225</td>
<td>0.490± 0.026</td>
<td>-0.433± 0.100</td>
<td>0.182± 0.076</td>
</tr>
<tr>
<td>$t_2(s)$</td>
<td>0.181± 0.019</td>
<td>0.312± 0.035</td>
<td>0.189± 0.033</td>
<td>0.203± 0.105</td>
</tr>
<tr>
<td>$A_3(V)$</td>
<td>0.886± 0.016</td>
<td>0.886± 0.016</td>
<td>0.577± 0.016</td>
<td>0.577± 0.016</td>
</tr>
<tr>
<td>$t_3(s)$</td>
<td>3.599± 0.334</td>
<td>3.599± 0.334</td>
<td>3.050± 0.410</td>
<td>3.050± 0.410</td>
</tr>
</tbody>
</table>

Table 4.7 Triple exponential decay fitting of Y in both linearly polarized (Figure 4.9) and circularly polarized (Figure 4.12) experiments.

By reexamining time constants in Table 4.4 and 4.5, we found the fast time constants in Y are very close to the slow time constants in X, which suggests that a comparable fast process as X must be suppressed in Y direction. A triple exponential decay fitting in Y direction recovers the same fast process as in X. The fitting parameters are shown in Table 4.7. Time constants are in bold. There are two distinct time constants found in X direction and three in Y direction. The first two time constants in Y direction are in good agreement with those in X direction respectively, which indicates the mechanisms for time constants $t_1$ and $t_2$ in Y should be the same as in X. Since Y direction differs from X direction in that Y is more mechanically constrained than X, the third time constant in Y direction must be associated with the mechanical spring constraint.
4.4.2 Empirical Solution

From experimental data fitting, $\theta$ is given by

$$\theta = A_0 + A_1 \exp \left( -\frac{t - t_0}{t_1} \right) + A_2 \exp \left( -\frac{t - t_0}{t_2} \right).$$  \hspace{1cm} (4.26)

Rewrite Equation 4.19 into the form,

$$\ddot{x} + \frac{4k_1 - 2k_2}{m} x = -\frac{4k_2 l}{m} \theta,$$  \hspace{1cm} (4.27)

and then substituting Equation 4.26 into Equation 4.27 yields,

$$\ddot{x} + \frac{4k_1 - 2k_2}{m} x = -\frac{4k_2 l}{m} \left[ A_0 + A_1 \exp \left( -\frac{t - t_0}{t_1} \right) + A_2 \exp \left( -\frac{t - t_0}{t_2} \right) \right].$$  \hspace{1cm} (4.28)

Letting $p = \frac{4k_1 - 2k_2}{m}$ and $q = -\frac{4k_2 l}{m}$, then Equation 4.28 becomes,

$$\ddot{x} + px = q \left[ A_0 + A_1 \exp \left( -\frac{t - t_0}{t_1} \right) + A_2 \exp \left( -\frac{t - t_0}{t_2} \right) \right].$$  \hspace{1cm} (4.29)

The general solution to Equation 4.29 is given by,

$$x = x_c + x_p.$$  \hspace{1cm} (4.30)

The complimentary solution is given by

$$x_c = c_1 e^{i\sqrt{p}t} + c_2 e^{-i\sqrt{p}t}. \hspace{1cm} (4.31)$$

A trial particular solution can be written as

$$x_p = a_0 + a_1 \exp \left( -\frac{t - t_0}{t_1} \right) + a_2 \exp \left( -\frac{t - t_0}{t_2} \right). \hspace{1cm} (4.32)$$

Substituting $x_c$ and $x_p$ into Equation 4.29 and comparing coefficients, we get

$$pa_0 - qA_0 = 0,$$

and $\frac{a_1}{t_1^2} + pa_1 - qA_1 = 0,$

and $\frac{a_2}{t_2^2} + pa_2 - qA_2 = 0.$
then

\[ a_0 = \frac{qA_0}{p}, \]
\[ a_1 = \frac{qA_1}{p + \frac{1}{t_1}}, \]
\[ a_2 = \frac{qA_2}{p + \frac{1}{t_2}}. \]

Putting it all together, the general solution is given by

\[
x = c_1 e^{i\sqrt{p}t} + c_2 e^{-i\sqrt{p}t}
+ \frac{qA_0}{p} + \frac{qA_1}{p + \frac{1}{t_1}} \exp \left( -\frac{t - t_0}{t_1} \right) + \frac{qA_2}{p + \frac{1}{t_2}} \exp \left( -\frac{t - t_0}{t_2} \right).
\]

(4.33)

The spring constant of the PMMA fiber is given by
\[ k_1 = \frac{AE}{l}, \]
and Young’s modulus of PMMA is typically from 1800 Mpa to 3100 Mpa, so,
\[ k_1 = \frac{AE}{l} = \frac{\pi (500 \mu m / 2)^2 \times 3 \times 10^9 N/m^2}{5 \text{ mm}} = \frac{3\pi}{8} \times 10^5 N/m, \]
which yields \(|p| \gg \frac{1}{t_1^2}\) and \(|p| \gg \frac{1}{t_2^2}\). Thus \(x\) is reduced to

\[
x = c_1 e^{i\sqrt{p}t} + c_2 e^{-i\sqrt{p}t}
+ \frac{q}{p} \left[ A_0 + A_1 \exp \left( -\frac{t - t_0}{t_1} \right) + A_2 \exp \left( -\frac{t - t_0}{t_2} \right) \right]
= c_1 e^{i\sqrt{p}t} + c_2 e^{-i\sqrt{p}t} + \frac{q}{p} \theta.
\]

(4.34)

Given that the oscillation of \(x\) goes to zero with infinite time, the first two terms on the right hand side of Equation 4.34 should be much much smaller than the last term if they are not zero. Thus it is reasonable to assume

\[ x \doteq \frac{q}{p} \theta = \frac{1}{1 - 2\frac{k_1}{k_2}} 2\theta. \]

(4.35)
4.4.3 Alternative Approach

θ can also be written as

\[ \theta = \frac{x - x'}{L_1 + L_2} \]

When \( x' \ll x \), \( \theta = \frac{x}{L_1 + L_2} \), then,

\[ x = (L_1 + L_2)\theta = 2l\theta. \tag{4.36} \]

4.5 Photothermal Heating

Polymer materials have properties similar to fluids when heated. Thus the heat transfer process within a polymer resembles a typical convective cooling process which can be modeled using Newton cooling.

In 1701, Isaac Newton suggested the convective cooling process would be governed by

\[ \frac{dT_{\text{body}}}{dt} \propto T_{\text{body}} - T_\infty, \tag{4.37} \]

where \( T_\infty \) is the temperature of the oncoming fluid or the equilibrium temperature[50].

If we substitute \( P_t \) and \( P_c \) of Equation 4.4 into Equation 4.2 and group coefficients to only have \( I_{pump} \) and \( n_t(n_c) \) as variables, the rate equation becomes,

\[ \frac{\partial n_t}{\partial t} = -\xi_1 I_{pump}n_t + \xi_2 I_{pump}n_c + \gamma n_c, \tag{4.38} \]

which will be used in the numerical simulations.

Applying Equation 4.3 to Equation 4.38 yields,

\[ \frac{\partial n_t}{\partial t} = -\xi_1 I n_t + \xi_2 I(N - n_t) + \gamma(N - n_t) \]

\[ = -[(\xi_1 + \xi_2)I + \gamma]n_t + (\xi_2 I + \gamma)N. \]
Thus the solution to the first-order rate equation is given by

\[ n_t = \exp \left[ - \int [\gamma + (\xi_1 + \xi_2)I]dt \right] \]

\[ \times \left\{ \int \exp \left[ \int [\gamma + (\xi_1 + \xi_2)I]dt \right] \times (\xi_2IN + \gamma N)dt + C \right\} \]

\[ = \exp \left[ -[\gamma + (\xi_1 + \xi_2)I]t \right] \times \left\{ \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I} \exp \left[ [\gamma + (\xi_1 + \xi_2)I]t \right] + C \right\} \]

\[ = \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I} + C \times \exp \left[ -[\gamma + (\xi_1 + \xi_2)I]t \right]. \]

Assuming the initial condition that cis and trans populations are the same, \( n_t(0) = \frac{1}{2}N \), and,

\[ n_t(0) = \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I} + C = \frac{1}{2}N. \]

Then,

\[ C = \frac{1}{2}N - \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I}, \]

and,

\[ n_t = \underbrace{\frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I}}_{A} + \underbrace{\frac{1}{2}N - \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I}}_{B} \times e^{-[\gamma + (\xi_1 + \xi_2)I]t} \]

\[ = \frac{1}{2}Ne^{-[\gamma + (\xi_1 + \xi_2)I]t} + \frac{\xi_2IN + \gamma N}{\gamma + (\xi_1 + \xi_2)I} \left( 1 - e^{-(\gamma + (\xi_1 + \xi_2)I)\cdot t} \right). \]

According to Bian[21], the heating rate for a fiber under uniform illumination is given by

\[ \frac{dT}{dt} + hT = \alpha n_t I. \] (4.39)
where $T$ is the temperature rise from equilibrium, $h$ is the cooling rate of the fiber and $\alpha$ is the temperature increase per trans molecule per unit of intensity per unit of time.

Substituting $n_t$ into the above equation, we get,

$$T = e^{-ht} \left[ \int e^{ht} (\alpha I A + \alpha I B e^{-\beta t}) dt + C \right]$$

$$= e^{-ht} \left\{ \int \left[ \alpha I A e^{ht} + \alpha I B e^{(h-\beta)t} \right] dt + C \right\}$$

$$= e^{-ht} \left\{ \frac{\alpha I A}{h} e^{ht} + \frac{\alpha I B}{h-\beta} e^{(h-\beta)t} + C \right\}$$

$$= \frac{\alpha I A}{h} + \frac{\alpha I B}{h-\beta} e^{-\beta t} + C e^{-ht}.$$

Since $T(0) = 0$,

$$T(0) = \frac{\alpha I A}{h} + \frac{\alpha I B}{h-\beta} + C = 0,$$

thus,

$$C = - \left( \frac{\alpha I A}{h} + \frac{\alpha I B}{h-\beta} \right),$$

and,

$$T = \frac{\alpha I A}{h} + \frac{\alpha I B}{h-\beta} e^{-\beta t} - \left( \frac{\alpha I A}{h} + \frac{\alpha I B}{h-\beta} \right) e^{-ht}$$

$$= \frac{\alpha I N (\xi_2 I + \gamma)}{h [\gamma + (\xi_1 + \xi_2) I]} + \frac{\alpha I}{h - [\gamma + (\xi_1 + \xi_2) I]} \left( \frac{1}{2} N - \frac{\xi_2 I N + \gamma N}{\gamma + (\xi_1 + \xi_2) I} \right)$$

$$\times e^{-\gamma + (\xi_1 + \xi_2) t}$$

$$- \left[ \frac{\alpha I N (\xi_2 I + \gamma)}{h [\gamma + (\xi_1 + \xi_2) I]} + \frac{\alpha I}{h - [\gamma + (\xi_1 + \xi_2) I]} \left( \frac{1}{2} N - \frac{\xi_2 I N + \gamma N}{\gamma + (\xi_1 + \xi_2) I} \right) \right] e^{-ht}.$$

The photomechanical response consists of two parts: $\Delta L/L$ due to photoisomerization, which is proportional to the difference between trans population and cis population, and photothermal heating, which is proportional to the temperature change
of the fiber. Thus,

\[ \frac{\Delta L}{L} = a(n_t - n_e) + bT \]  

(4.40)

\[ = a(2n_t - N) + bT \]

\[ = a(2A + 2Be^{-\beta t} - N) + b \left[ \frac{\alpha I_A}{h} + \frac{\alpha I_B}{h - \beta} e^{-\beta t} - \left( \frac{\alpha I_A}{h} + \frac{\alpha I_B}{h - \beta} \right) e^{-ht} \right] \]

\[ = \left( 2aA - aN + \frac{\alpha IA}{h} \right) + B \left( 2a + \frac{\alpha I_B}{h - \beta} \right) e^{-\beta t} - b \left( \frac{\alpha IA}{h} + \frac{\alpha IB}{h - \beta} \right) e^{-ht}. \]
Chapter 5

Numerical Analysis

5.1 Thermal Analysis

5.1.1 Introduction

Heat transfer can take the form of heat conduction, convection, and radiation. In most solid materials, heat conduction plays the dominant role.

5.1.2 Fourier’s Law of Heat Conduction

Fourier’s law, an empirical law governing thermal conduction described by Joseph Fourier in 1822, states that the heat flux, \( q(W/m^2) \), resulting from thermal conduction is proportional to the magnitude of the temperature gradient and opposite to it in sign, which can be written as[50]

\[
q = -k \frac{\partial T}{\partial x}.
\]

(5.1)

The constant of proportionality, \( k \), is called the thermal conductivity. It has the dimension \( W \cdot m^{-1} \cdot K^{-1} \). Fourier’s law in three-dimensional form is given by

\[
\vec{q} = -k \nabla T.
\]

(5.2)
in which $\nabla T$ is the temperature gradient and has the form

$$\nabla T \equiv \hat{i} \frac{\partial T}{\partial x} + \hat{j} \frac{\partial T}{\partial y} + \hat{k} \frac{\partial T}{\partial z}.$$ 

Next is the derivation of the heat equation.

Consider a three-dimensional region $R$, enclosed by surface $S$. $\vec{n}$ is the surface normal of unit area pointing outwards and $dS$ is the magnitude of the area element. The heat flowing out of $dS$ is $\vec{q} \cdot (\vec{n}dS)$ or $(-k\nabla T) \cdot (\vec{n}dS)$. Thus the total heat flow out of region $R$ through surface $S$ is given by

$$\int_S (-k\nabla T) \cdot (\vec{n}dS). \quad (5.3)$$

For a heat source inside $R$, the heat generated within the region is $\int_R \dot{q}dR$. The overall heat increase in $R$ is the addition of the heat flow into $R$ across surface $S$ and the heat generated within $R$, given by

$$Q = -\int_S (-k\nabla T) \cdot (\vec{n}dS) + \int_R \dot{q}dR. \quad (5.4)$$

The thermal energy increase in region $R$ is then

$$\frac{dU}{dt} = \int_R \left( \rho c \frac{\partial T}{\partial t} \right) dR, \quad (5.5)$$

where $\rho$ and $c$ are the density and specific heat of the material, respectively.

In an incompressible medium,

$$Q = \frac{dU}{dt}. \quad (5.6)$$

Substituting $Q$ and $dU/dt$ into Equation 5.6 yields

$$-\int_S (-k\nabla T) \cdot (\vec{n}dS) + \int_R \dot{q}dR = \int_R \left( \rho c \frac{\partial T}{\partial t} \right) dR,$$

or, after regrouping terms,

$$\int_S k\nabla T \cdot \vec{n}dS = \int_R \left[ \rho c \frac{\partial T}{\partial t} - \dot{q} \right] dR. \quad (5.7)$$
Equation 5.7 consists of a surface integral on the left hand side and a volume integral on the right hand side. **Gauss’s theorem** converts the surface integral into a volume integral,

\[ \int_S \vec{A} \cdot \vec{n} dS = \int_R \nabla \cdot \vec{A} dR \]  

(5.8)

So, the LHS of Equation 5.7 becomes \( \int_R \nabla \cdot (k \nabla T) dR \), reducing Equation 5.7 to

\[ \int_R \left[ \nabla \cdot (k \nabla T) - \rho c \frac{\partial T}{\partial t} + \dot{q} \right] dR = 0. \]  

(5.9)

Since region \( R \) is randomly chosen, Equation 5.9 must hold for all arbitrary region \( R \), i.e., the integrand must vanish, which gives,

\[ \nabla \cdot (k \nabla T) + \dot{q} = \rho c \frac{\partial T}{\partial t}, \]  

(5.10)

where \( \nabla \cdot (k \nabla T) = \nabla \cdot (\nabla k \cdot \nabla T + k \nabla \cdot \nabla T) \).

In general, the thermal conductivity \( k \) is a function of position and temperature, \( k = k(\vec{r}, T(\vec{r}, t)) \). If the material of interest is homogeneous, \( k \) only depends on temperature, i.e., \( k = k(T(t)) \). If the variation of \( k \) with \( T \) is small within the temperature range and spatial region of interest, \( k \) can be treated approximately as a constant, in which case Equation 5.10 becomes

\[ \nabla^2 T + \frac{\dot{q}}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}, \]  

(5.11)

where \( \alpha \equiv \frac{k}{\rho c} \) is the **thermal diffusivity**. The physical dimensions of relevant coefficients are given by

\[ 77 \]
5.1.3 Heat Conduction in 1D with no Heat Source

We first consider the one-dimensional homogeneous heat equation which contains no heat source

$$\frac{\partial^2 T}{\partial x^2} = \frac{1}{\alpha} \frac{\partial T}{\partial t}. \quad (5.12)$$

Normally one solves Equation 5.12 by separating variables, but in the situation where the temperature distribution $T$ does not depend separately on $x$ and $t$, a composite variable $\xi = x/(2\alpha t)^{1/2}$ can be substituted to solve the heat equation[51].

Since equation 5.12 is dimensionally homogeneous, by properly choosing characteristic constants, the variables on both sides of the equation can be converted into dimensionless arguments, which usually can significantly reduce the complexity of the problem.
By introducing characteristic length \( X \), the dimensionless length is \( x/X \). Similarly, the dimensionless temperature is \( T/T_c \). While \( X \) and \( T_c \) are normally determined from boundary parameters, there exists no characteristic time for most scenarios. In such cases, it is useful to use \( \alpha t/X^2 \) to represent the dimensionless time. Thus,

\[
\frac{T}{T_c} = f \left( \frac{x \alpha t}{X^2} \right) .
\] (5.13)

If the problem contains no characteristic length in its boundaries, the solution must depend on the product of \( (x/X)^a \) and \( \alpha t/X^2 \), or just equivalently \( \alpha t/x^2 \). So the solution becomes

\[
\frac{T}{T_c} = f \left( \frac{\alpha t}{x^2} \right) \quad \text{or} \quad \frac{T}{T_c} = f \left( \frac{x}{\sqrt{4\alpha t}} \right) .
\] (5.14)

Introducing the new composite variable \( \xi = x/(4\alpha t)^{1/2} \), the temperature becomes

\[
T(x, t) = \Theta \left( \frac{x}{\sqrt{4\alpha t}} \right) = \Theta(\xi) .
\] (5.15)

then

\[
\frac{\partial T}{\partial t} = \frac{\partial \Theta}{\partial \xi} \frac{\partial \xi}{\partial t} = -\frac{x}{4\sqrt{\alpha} t^3} \frac{\partial \Theta}{\partial \xi} ,
\]

\[
\frac{\partial T}{\partial x} = \frac{\partial \Theta}{\partial \xi} \frac{\partial \xi}{\partial x} = \frac{1}{2\sqrt{\alpha} t} \frac{\partial \Theta}{\partial \xi} , \quad \text{and} \quad \frac{\partial^2 T}{\partial x^2} = \left( \frac{\partial \Theta}{\partial x} / \partial \xi \right) \frac{\partial \xi}{\partial x} = \frac{1}{4\alpha t} \frac{\partial^2 \Theta}{\partial \xi^2} .
\] (5.16)

Substituting Equation 5.16 into Equation 5.12, one finds,

\[
\Theta'' + 2\xi \Theta' = 0,
\] (5.17)

where \( \Theta' \equiv \frac{\partial \Theta}{\partial \xi} \).

The above approach turns a partial differential equation into an ordinary differential equation which only requires boundary conditions. The solution to equation 5.17 possesses the general form

\[
\Theta = C_1 \int_0^{x/(4\alpha t)^{1/2}} exp(-\xi^2) d\xi + C_2
\]

\[
\equiv \frac{\sqrt{\pi}}{2} C_1 \text{erf} \left( \frac{x}{\sqrt{4\alpha t}} \right) + C_2 ,
\] (5.18)
where \( \text{erf} \) represents \textit{Guass’s Error Function}, given by,
\[
\text{erf}(x) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt,
\]
where \( \text{erf}(0) = 0, \text{erf}(\pm \infty) = \pm 1, \text{erf}(-x) = -\text{erf}(x), \text{erfc}(x) \equiv 1 - \text{erf}(x). \)

\( C_1 \) and \( C_2 \) in Equation 5.18 are determined by the boundary and initial conditions. For the following boundary(b.c.’s) and initial(i.c.’s) conditions for \( T \),
\[
T = \begin{cases} 
T_c & \text{for } x > 0, \ t = 0 \\
-T_c & \text{for } x < 0, \ t = 0 \\
0 & \text{for } x = 0, \ t > 0,
\end{cases}
\]
(5.19)

which then translates into boundary condition for \( \Theta \),
\[
\Theta = \begin{cases} 
\pm T_c & \text{for } \xi = \pm \infty \\
0 & \text{for } \xi = 0,
\end{cases}
\]
(5.20)

we get \( C_2 = 0, C_1 = 2T_c/\sqrt{\pi} \) and
\[
T/T_c = \frac{2}{\sqrt{\pi}} \int_{0}^{x/\sqrt{4\alpha t}} e^{-\xi^2} d\xi \equiv \text{erf} \left( \frac{x}{\sqrt{4\alpha t}} \right)
\]
(5.21)

Equation 5.21 satisfies boundary condition of the first kind. Because the heat equation 5.12 is linear and homogeneous, the derivatives of Equation 5.21 are also solutions to the heat equation, which can be easily verified.

5.1.4 Heat Conduction in 1D with Transient Heat Source

Consider the case where at time \( t = 0 \) and at a point \( r = 0 \), an enthalpy \( H_0 \) is released in an extended, homogeneous, and isotropic medium. This process may be fast or slow and may or may not depend on \( x \) and \( t \) separately. We begin by using a tentative
solution based on Section 5.1.3

\[ T(r, t) = \exp(-\xi^2) \times f(t), \quad (5.22) \]

and \( \xi = \frac{r}{\sqrt{4\alpha t}}. \)

Here, \( T(r, t) \) is the excess temperature over the initial temperature, i.e., \( \Delta T \). For simplicity, we assume \( T_0 = 0 \).

Since this is not a continuous heat source, no additional heat will be generated. According to energy conservation, heat must be recovered at every instant of time in the form of an increase in the enthalpy of the medium. For an infinitesimal region, this increment is given by

\[ c\Delta mT = c\rho\Delta VT = c\rho AdrT, \quad (5.23) \]

where \( \Delta m, \Delta V \) are the mass and volume of the region, and \( A \) is the cross section area.

We integrate over the semi-infinite region which collects half of the total enthalpy released

\[ \int_0^\infty (c\rho AdrT) = \int_0^\infty c\rho AT(r, t)dr = \frac{H_0}{2}. \quad (5.24) \]

Substituting the tentative solution Equation 5.22 into Equation 5.24 yields

\[ \frac{H_0}{2} = \int_0^\infty c\rho A\exp(-\xi^2) \times f(t)dr \\
= c\rho A\sqrt{4\alpha t} \times f(t) \int_0^\infty \exp(-\xi^2)d\xi. \quad (5.25) \]

By applying Gauss’s Integral,

\[ \int_{-\infty}^{\infty} \exp(-x^2) = \sqrt{\pi} \quad \text{and} \quad \int_0^{\infty} \exp(-x^2) = \frac{\sqrt{\pi}}{2}, \quad (5.26) \]

Equation 5.25 becomes

\[ \frac{H_0}{2} = c\rho A\sqrt{4\alpha t} \times f(t)\frac{\sqrt{\pi}}{2} \implies f(t) = \frac{H_0}{\rho c A\sqrt{4\pi \alpha t}}. \quad (5.27) \]
So the solution to the one-dimensional heat equation without a heat source is given by

\[ T(r, t) = \frac{H_0}{\rho c A \sqrt{4\pi \alpha t}} \exp \left( -\frac{r^2}{4\alpha t} \right), \]

which satisfies boundary condition of the first kind.

### 5.1.5 Heat Conduction in 1D with Continuous Heat Source

#### Infinitesimal Heat Source

If the heat source changes continuously at a rate \( \dot{Q}(t) \), we can use an infinitesimal time interval \( d\tau \) then apply it to the previous result. During the time period from \( t = \tau \) to \( t = \tau + d\tau \), the heat released is \( \dot{Q}(t)d\tau \). This infinitesimal time period resembles the transient heat problem. Since the Laplace heat equation is linear, the solution to this continuous heating problem can be interpreted as a superposition of the solutions to each infinitesimal time interval, which is given by

\[
T(r, t) = \int_0^t \frac{\dot{Q}(t)}{\rho c A \sqrt{4\pi \alpha (t - \tau)}} \exp \left( -\frac{r^2}{4\alpha (t - \tau)} \right) d\tau
= \frac{1}{\rho c A \sqrt{4\pi \alpha}} \int_0^t \frac{\dot{Q}(t)}{\sqrt{t - \tau}} \exp \left( -\frac{r^2}{4\alpha (t - \tau)} \right) d\tau.
\]

(5.29)

Substituting

\[
\psi = \frac{r}{\sqrt{4\alpha (t - \tau)}}, \quad d\tau = \frac{r^2}{2\alpha \psi^3} d\psi
\]

(5.30)

into the above equation, we get

\[
T(r, t) = \frac{1}{\rho c A \sqrt{\pi}} \int_{r/(4\alpha t)^{1/2}}^{\infty} \dot{Q}(t) \exp(-\psi^2) \frac{r}{2\alpha \psi^2} d\psi
= \frac{r}{2\alpha \rho c A \sqrt{\pi}} \int_{r/(4\alpha t)^{1/2}}^{\infty} \dot{Q}(t) \frac{\exp(-\psi^2)}{\psi^2} d\psi
= \frac{r}{2k \rho c A \sqrt{\pi}} \int_{r/(4\alpha t)^{1/2}}^{\infty} \dot{Q}(t) \frac{\exp(-\psi^2)}{\psi^2} d\psi.
\]

(5.31)
If the heating rate $\dot{Q}(t)$ is constant, Equation 5.31 reduces to

$$T(r, t) = \frac{r\dot{Q}}{2kA\sqrt{\pi}} \int_{r/(4\alpha t)^{1/2}}^{\infty} \frac{exp(-\psi^2)}{\psi^2} d\psi. \quad (5.32)$$

The integral in Equation 5.32 is of the form,

$$\int_{x}^{\infty} \frac{e^{-x^2}}{x^2} dx = \frac{1}{x} e^{-x^2}|_{x=\infty} - 2 \int_{x}^{\infty} e^{-x^2} dx$$

$$= \frac{1}{x} e^{-x^2}|_{x=\infty} - \sqrt{\pi} \left( \frac{2}{\sqrt{\pi}} \int_{x}^{\infty} e^{-x^2} dx \right)$$

$$= \sqrt{\pi} \left[ \frac{1}{\sqrt{\pi}x} e^{-x^2} - \text{erfc}(x) \right]. \quad (5.33)$$

Substituting Equation 5.33 into Equation 5.32, we get the final form,

$$T(r, t) = \frac{r\dot{Q}}{2kA} \left[ \frac{1}{\sqrt{\pi}x} e^{-x^2} - \text{erfc}(x) \right]_{x=r/(4\alpha t)^{1/2}}$$

$$= \frac{r\dot{Q}}{2kA} \left[ \frac{\sqrt{4\alpha t}}{\sqrt{\pi}r} exp\left(-\frac{r^2}{4\alpha t}\right) - \text{erfc}\left(\frac{r}{\sqrt{4\alpha t}}\right) \right], \quad (5.34)$$

which is solution to the problem with continuous heat source of constant heating rate. For cases with a changing heating rate, Equation 5.31 must be used to solve the problem.

**Finite Heat Source**

The previous discussion considers a heat source with infinitesimal dimensions, e.g., point source, thin-layered source. If the heat source extends over finite dimensions, e.g., a laser beam penetrating a finite depth into an optical fiber, we can use a finite element approach to tackle the problem.

If a laser beam is launched into a dye-doped polymer fiber along its center axis, at least the 1/e optical absorption length of the total fiber length from the incident side should be considered as a heat source, under the condition that the laser light is not strongly absorbed by the fiber material. Otherwise, a point/thin-layered source treatment can be used.
In a finite element approach, we can divide the $1/e$ length into multiple thin-layered sources with thickness $\Delta x$. The thermal contribution from each thin-layered source can be calculated independently, and the total thermal effect is the sum of thermal effects from all the discrete sources, which is shown schematically in Figure 5.1.

\[ \sum \]

**Figure 5.1** Finite element decomposition of a laser source that heats a fiber. Heat is shown flowing to the right.
5.2 Modeling

In Section 4.5, Newton cooling was used to derive a less rigorous analytical expression of the photothermal heating contribution to the photomechanical response. In this section, a numerical simulation using the more accurate Fourier’s Law is carried out.

Recall Heat Equation 5.11,
\[ \nabla^2 T + \frac{\dot{q}}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}, \]  
(5.11)

and Rate Equation 4.38,
\[ \frac{\partial n_t}{\partial t} = -\xi_1 I_{pump} n_t + \xi_2 I_{pump} n_c + \gamma n_c. \]  
(4.38)

In our experiment, absorbed laser irradiation is the heat source. Then \( \dot{q} \) is proportional to the instantaneous laser intensity \( I_{pump} \). On the other hand, \( \dot{q} \) also depends on the number of absorbers. To proceed, we make the following assumptions:

1. \( \dot{q} \) is proportional to the instantaneous laser intensity, i.e., \( \dot{q} \propto I_{pump} \);
2. Only trans molecules absorb laser light and absorption by cis molecules is ignored, i.e., \( \dot{q} \propto n_t \);
3. Absorption by PMMA is ignored;
4. Rotational energy is ignored.

An alternative view is as follows: \( \dot{q} \) depends on the number of absorbers and the probability of absorption of a photon by an absorber in Rate Equation 4.2. To first order approximation, \( \dot{q} \propto P_t n_t \). Since \( P_t \) is proportional to \( I_{pump} \), \( \dot{q} \propto I_{pump} n_t \).

Thus Heat Equation 5.11 can be rewritten as
\[ \nabla^2 T + \frac{\beta_1 I_{pump} n_t}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}, \]  
(5.35)
where $\beta_1$ is a proportionality constant.

In Section 5.1.3, a boundary condition of the first kind is used which requires boundary temperature information. However, in the case of applying a specified heat flux $q_w$, e.g., deposited by a laser beam of constant intensity, at the boundary of a semi-infinite region, i.e., at the end of a dye-doped polymer fiber, the temperature at the incident boundary is no longer constant and not directly identifiable. Thus we need to seek an alternative approach. As mentioned in Section 5.1.3, the derivatives of a solution to the Heat Equation are also solutions to the Heat Equation. Thus we first differentiate the one dimensional Heat Equation with respect to $x$,

$$\frac{\partial^3 T}{\partial x^3} = \frac{1}{\alpha} \frac{\partial^2 T}{\partial t \partial x}.$$  \hspace{1cm} (5.36)

Then we substitute Fourier’s Law, $q = -k\partial T/\partial x$, into Equation 5.36 to get the Heat Flux Equation[50],

$$\frac{\partial^2 q}{\partial x^2} = \frac{1}{\alpha} \frac{\partial q}{\partial t},$$  \hspace{1cm} (5.37)

with b.c.’s and i.c.’s given by

$$q = \begin{cases} 
q_w & \text{for } x = 0, t > 0 \\
0 & \text{for } x \geq 0, t = 0.
\end{cases}$$  \hspace{1cm} (5.38)

We have transformed the heat flux problem into a similar form of the heat problem solved in Section 5.1.3, which yields

$$q = q_w \left[ 1 - \text{erf} \left( \frac{x}{\sqrt{4\alpha t}} \right) \right] = q_w \cdot \text{erfc} \left( \frac{x}{\sqrt{4\alpha t}} \right)$$  \hspace{1cm} (5.39)

Substituting Equation 5.39 into Fourier’s Law and integrating both sides from the
incident boundary, we get
\[ T_w = T_\infty + \frac{q_w}{k} \int_0^\infty \text{erfc}(\frac{x}{\sqrt{4\alpha t}})dx \]
\[ = T_\infty + \frac{q_w\sqrt{4\alpha t}}{k} \int_0^\infty \text{erfc}(x')dx' \]
\[ = T_\infty + 2 \frac{q_w}{k} \sqrt{\frac{\alpha t}{\pi}}, \quad (5.40) \]

where the following error function integral is used[52]
\[ \int_0^\infty \text{erfc}(x)dx = \frac{1}{\sqrt{\pi}}. \]

Equation 5.40 gives the boundary condition for \( T \) at the fiber end under laser excitation. At the other end, the boundary condition of the third kind must be used
\[ -k \frac{\partial T}{\partial x} \bigg|_{x=L} = \bar{h}(T - T_\infty)_{x=L}. \quad (5.41) \]
The LHS represents the heat conduction at the interior of the boundary, and the RHS represents the heat convection at the exterior of the boundary. Thus we have found the boundary and initial conditions for the problem in Heat Equation 5.35:

\[ \text{i.c.} \quad T = T_0 \quad \text{for all } x \text{ at } t = 0 \quad (5.42) \]

\[ \text{b.c.} \quad \begin{cases} 
T = T_\infty + 2 \frac{q_w}{k} \sqrt{\frac{\alpha t}{\pi}} & \text{for } x = 0 \\
-k \frac{\partial T}{\partial x} = \bar{h}(T - T_\infty) & \text{for } x = L 
\end{cases} \quad (5.43) \]

Since we designate \( T \) as the difference between current and initial temperature, \( T_0 \) and \( T_\infty \) can be set to ZERO.

So far we have found two relations, i.e., Rate Equation 4.38 and Heat Equation 5.35, for three physical quantities, \( T, n_t, I_{\text{pump}} \). Thus we need to find a third relation
so that the three can be expressed in terms of the two independent variables, \( x \), and \( t \).

**Beer-Lambert’s Law** states the absorption of light is an exponential function of the material’s absorbance and propagation distance. If we consider a infinitesimal length segment \( dx \) along the light path inside the fiber and designate \( dI \) as the light absorbed in that segment, we have \( dI \propto dx \) and \( dI \propto n_t I \), which combines to

\[
dI = -\beta_2 n_t I dx, \tag{5.44}
\]

where \( \beta_2 \) is a proportionality coefficient and the negative sign represents absorption.

In Section 4.3, we found thermal cis-trans isomerization is the dominate mechanism of the length change of the dye-doped polymer fiber. Since thermal isomerization is temperature dependent, we need another relation to connect these two in our modeling.

In 1889, Swedish physicist-turned-chemist *Svante August Arrhenius* proposed a formula for the dependence of the rate constant of a chemical reaction on temperature known as the **Arrhenius Equation**[40]:

\[
k = Ae^{-E_a/RT}, \tag{5.45}
\]

where \( k \) is the rate constant, \( E_a \) the activation energy of the reaction, \( R \) the gas constant, and \( T \) the absolute temperature. Equation 5.45 states that the rate constant decreases with increasing activation energy and increases with increasing temperature.
Putting this all together yields

\[
\frac{\partial n_t}{\partial t} = -\xi_1 I n_t + \xi_2 I n_c + \gamma n_c, \tag{4.38}
\]

\[
n_t + n_c = N, \tag{4.3}
\]

\[
\nabla^2 T + \frac{\beta_1 I n_t}{k} = \frac{1}{\alpha} \frac{\partial T}{\partial t}, \tag{5.35}
\]

\[
dI = -\beta_2 n_t I dx, \tag{5.44}
\]

and \( \gamma = Ae^{-E_a/RT} \), \tag{5.45}

with b.c.’s and i.c.’s:

\[
T = 2q_w \sqrt{\frac{\alpha t}{\pi}} \quad \text{for } x = 0, \tag{5.46}
\]

\[
-k \frac{\partial T}{\partial x} = \bar{h}T \quad \text{for } x = L, \tag{5.47}
\]

and \( T = 0 \) for \( t = 0 \). \tag{5.48}

\section*{5.3 Numerical Results}

In the modeling, a 10 second simulation of a 5mm long fiber is divided into 250 spatial steps, and 10,000 time steps, starting at room temperature 300\( K \). The incident laser beam is turned on at zero second. The absorption coefficient is acquired from a DR1/PMMA thin film measurement described in AppendixA. The thermal activation energy of cis-trans isomerization used is 23kcal/mol\[53, 54\]. Numerical simulations with high and low pump intensities are carried out.
Figure 5.2 Calculated intensity distribution in the fiber as a function of time over a 10 second time interval after the laser is turned on.
5.3.1 High Pump Intensity

For a pump intensity of $5 \times 10^4 W/m^2$ at the input end face of the dye-doped polymer fiber, Figure 5.2 shows the intensity distribution inside the fiber over a time period of 10 second after the laser is turned on. The laser intensity quickly decreases to zero due to strong absorption by the dye-doped polymer fiber. The heat generated by the laser light then raises the temperature of the fiber, resulting in a temperature profile shown in Figure 5.3.

![Graph showing temperature increase over time and distance.]

Figure 5.3 Calculated temperature increase in a fiber as a function of time after the laser source is turned on.

Figure 5.4 shows the number density distribution of trans-DR1 molecules. The reaction rate of cis to trans thermal isomerization is temperature dependent, and it increases as temperature increases. At the early stage of laser heating, the temperature increase is small and the rate of trans to cis photoisomerization is bigger than the rate of cis to trans thermal isomerization. Thus the population of trans molecules
Figure 5.4 Calculated number density of trans-DR1 molecules as a function of time after the pump laser is turned on in a dye-doped fiber. The population of trans-DR1 molecules at $X = 0$ mm first decreases and then increases to a high point.

decreases. When the temperature increases to a point that the rate of cis to trans thermal isomerization starts to outrun that of trans to cis photoisomerization, the population of trans molecules starts to increase.

Furthermore, over time, the population of trans molecules accumulates near the input end face of the fiber, due to the temperature increase induced by laser heating. This increase of the number of absorbers, in turn, results in a deeper decrease of light intensity as can be seen at the far end of the time axis in Figure 5.2(a) and 5.2(b), which reflects the coupled nature of this complex process.
5.3.2 Low Pump Intensity

The low pump intensity limit is calculated using a pump intensity of $5 \times 10^2 \text{W/m}^2$ at the input end face of the dye-doped polymer fiber. Figure 5.5 shows the temperature distribution, and Figure 5.6 shows the intensity distribution inside the fiber. In contrast to Section 5.3.1, the laser intensity used in this case is not large enough to elevate the fiber temperature enough to increase the cis to trans thermal isomerization rate to overrun that of trans to cis photoisomerization. Thus in general, the population of trans molecules decreases as shown in Figure 5.7.

![Figure 5.5](image)

**Figure 5.5** Calculated temperature increase in a fiber as a function of time after the laser source is turned on.
Figure 5.6 Calculated intensity distribution in the fiber as a function of time over a 10 second time interval after the laser is turned on.
Figure 5.7 Calculated number density of \textbf{trans-DR1} molecules as a function of time after the pump laser is turned on in a dye-doped fiber. The laser intensity is not large enough to elevate the fiber temperature enough to increase the cis to trans thermal isomerization rate to overrun that trans to cis photoisomerization, resulting a decrease of the \textbf{trans} molecule population.
5.3.3 Results and Discussions

Section 5.3.1 and 5.3.2 give the numerical simulation results of temperature and number density of dye molecules. Thus the total photomechanical response of the dye-doped polymer fiber can be estimated by adding together the thermal contribution of the polymer matrix and the isomerization contribution of the dye molecules (Equation 4.40), giving,

$$\frac{\Delta L}{L} = a(n_t - n_c) + bT.$$

In Section 5.3.1, the decrease of trans molecule population due to trans to cis photoisomerization is heavily suppressed by the increase caused by cis to trans thermal isomerization. Together with thermal expansion of the polymer matrix, the overall photomechanical response leads to fiber elongation. This case is illustrated in Figure 5.8.

![Figure 5.8](image)

**Figure 5.8** Strain as a function of time for high pump intensity. (left) Isomerization contribution, (middle) temperature contribution, (right) total response.
However, if the incident intensity is attenuated to a level at which the reaction rate of thermal-induced isomerization is well below that of photoinduced isomerization, the decrease of trans molecule population will result in a fast contraction until the thermal expansion of the polymer matrix outruns the effects of photoisomerization. This case is illustrated in Figure 5.9.

Figure 5.9 Strain as a function of time for low pump intensity. (left) Isomerization contribution, (middle) temperature contribution, (right) total response.

Thus, in order to make the contraction observable, the incident intensity must be reduced appropriately.

The findings in Section 4.3 show the use of ND filters to lower the intensity did not lead to the observation of contraction. Since external attenuation to lower intensity greatly decreases the signal to noise ratio, to preserve an acceptable signal to noise ratio, the attenuation must be brought closer to the target molecules to convert the absorbed light to heat.
Black ink is applied directly to the input end face of the fiber to affect direct surface heating. Examined under an optical microscope, the ink layer encloses miniaturized pinholes which only pass a minuscule amount of light, but blocking most of it. This sample gives the predicted degree of contraction, and the resulting photomechanical response is shown in Figure 5.10.

![Figure 5.10](image)

**Figure 5.10** Measured photomechanical response of a fiber in which the front end is coated with black ink to absorb the pump light and affect surface heating. The fiber contracts as predicted by numerical calculations.

### 5.3.4 Summary

In this section, we developed a theory of coupled thermal/photoisomerization mechanism and showed that it predicts the change in fiber length for high pump intensity. To mimic the low intensity limit, we painted the input end of the fiber with black ink, and find that laser-induced surface heating leads to the correct behavior.
Chapter 6

Conclusions

In this work, we have studied the dynamics of the trans-cis photoisomerization mechanism of a DR1 doped PMMA polymer fiber in the waveguide configuration under UV light illumination at a wavelength of 355nm. A three-point-contact optically-actuated beam-controlling tilt mount was made of the target polymer fiber to measure the photomechanical response. Numerical simulation was used to model the dynamics of optically- and thermally-induced isomerization.

The experimental findings show that the fiber elongates upon UV irradiation under high intensities. The elongation process is described by a double exponential decay function, which includes a fast and a slow processes. The slow process is largely due to the thermal-diffusion-caused thermal expansion of the substrate polymer matrix. The mechanisms contributing to the fast processes originate from photoisomerization and thermal isomerization of the dye molecules. Under high pump intensities, the trans-cis photoisomerization in the UV band is overwhelmed by the thermally stimulated cis-trans isomerization, resulting in an overall elongation which is associated with the fast process. The experimental results with an externally attenuated pump intensity also shows an overall elongation.
The numerical simulation takes into account photoisomerization and the temperature-dependent thermal isomerization process as well as the heat diffusion problem studied by Dawson et al[55]. The coupled model shows that under high pump intensity, trans-cis photoisomerization decreases the trans molecule population near the input end of the fiber during the turn-on period of pump illumination. With constant laser heating at the end of the fiber, the internal temperature rises quickly and increases the reaction rate of thermal cis-trans isomerization, which results in an inversion/increase of the trans molecule population. The population of trans molecules quickly overruns that of cis molecules by a large amount, leading to net elongation. Under low pump intensity, the reaction rate of cis-trans thermal isomerization near the input end of the fiber is well below that of trans-cis photoisomerization, which results in a significant amount of decrease of the trans molecule population.

The numerical results provide a partial explanation to the mechanisms behind the observed photomechanical response, and also provide guidance to reexamine the experimental technique to recover the direct trans-cis photoisomerization contribution. When the pump beam is controlled using external attenuation, heat does not flow into the sample so that the thermal contribution is suppressed. The on-target attenuation method utilizes black ink to paint the fiber end to block most of the incident laser intensity but to allow conversion of light into heating of the fiber end. The resulting response shows behavior in the fast process, which is indication of contraction.

The current experimental and theoretical findings show temperature related effects contribute significantly to the photomechanical response in the trans-cis dynamics. Further investigations in low temperature limit or constant temperature condition when thermal effects are absent should provide a better understanding of direct trans-cis photoisomerization dynamics.
Appendix A

Samples

The samples under study are dye-doped polymer optical fiber. Here we review the typical properties of the samples used for experimentation.

Figure A.1 Absorbance spectrum of 0.5% DR1 doped PMMA fiber sample
To measure optical absorbance, the 8mg 0.5% DR1 doped PMMA fiber sample is squeezed at elevated temperature between two glass slides to 30µm thickness. The reference is a 13mg PMMA powder squeezed between two glass slides to 70µm thickness.

The peak absorption is at 490.11nm with an absorbance of 1.625. Absorbance at 355nm and 632nm are 0.162 and 0.005, respectively, where we used Beer-Lambert’s law,

\[ A = -\log_{10} \left( \frac{I}{I_0} \right) \] (A.1)

The average diameter of the fiber is 475µm, and the power of the 355nm pump laser light is 12mW. Assuming the entire laser beam is focused onto the fiber end, then the intensity is given by

\[ I_0 = \frac{12mW}{\pi \times \left( \frac{475\mu m}{2} \right)^2} = 6.8 \times 10^3 mW/cm^2. \] (A.2)

Since \( A = \alpha d \), the absorbance per unit length is,

\[ \alpha = \frac{1.625}{30\mu m} = 0.05417/\mu m \text{ at } 490nm. \]

\[ \alpha = \frac{0.162}{30\mu m} = 0.0054/\mu m \text{ at } 355nm. \]

\[ \alpha = \frac{0.005}{30\mu m} = 1.667 \times 10^{-4}/\mu m \text{ at } 632nm. \]

According to Beer-Lambert’s Law A.1, the intensity, \( I \), exiting a 5mm fiber is given by,

\[ I = I_0 \times 10^{-\alpha d} \] (A.3)

\[ = 6.8 \times 10^3 mW/cm^2 \times 10^{-0.0054/\mu m \times 5mm} \] (A.4)

\[ = 6.8 \times 10^{-24} mW/cm^2. \] (A.5)
Appendix B

Quadrant Photodiode

Under uniform illumination, the operation of a quadrant photodiode can be visualized as shown in Figure B.1:

![Quadrant Photodiode Diagram](image_url)

**Figure B.1** Quadrant photodiode
In Figure B.1, \( a \) is the gap width between adjacent quadrants, \( r \) is the radius of the beam spot, and the hatched area represents the light intensity that is lost in the gap. Thus the total effective detection area should be the non-hatched area enclosed by the beam spot.

Since \( a \) is very small compared with device dimension, the hatched area can be represented simply by rectangles. And it is easy to verify that

\[
\text{Sum} = \pi r^2 - 2(\sqrt{r^2 - x^2} + \sqrt{r^2 - y^2})a + a^2 \tag{B.1}
\]

\[
\text{Sum}_{\text{min}} = \text{Sum}(x = 0, y = 0) = \pi r^2 - 4ra + a^2 \tag{B.2}
\]

And

\[
A_{x-} = \frac{1}{2}(2\pi - \theta_x)r^2 - x\sqrt{r^2 - x^2} - (\sqrt{r^2 - y^2} - x)a \tag{B.3}
\]

\[
A_{x+} = \frac{1}{2}(2\pi - \theta_x)r^2 + x\sqrt{r^2 - x^2} - (\sqrt{r^2 - y^2} + x)a \tag{B.4}
\]

\[
A_{y-} = \frac{1}{2}(2\pi - \theta_y)r^2 - y\sqrt{r^2 - y^2} - (\sqrt{r^2 - x^2} - y)a \tag{B.5}
\]

\[
A_{y+} = \frac{1}{2}(2\pi - \theta_y)r^2 + y\sqrt{r^2 - y^2} - (\sqrt{r^2 - x^2} + y)a \tag{B.6}
\]

\[
\theta_x = 2\cos^{-1}\frac{x}{r} \tag{B.7}
\]

\[
\theta_y = 2\cos^{-1}\frac{y}{r} \tag{B.8}
\]

where \( \theta_x = \angle POQ \) and \( \theta_y = \angle MON \), both counter-clockwise.

Thus

\[
A_{x+} - A_{x-} = (\pi - \theta_x)r^2 + 2x\sqrt{r^2 - x^2} - 2ax
\]

\[
= (\pi - 2\cos^{-1}\frac{x}{r})r^2 + 2x\sqrt{r^2 - x^2} - 2ax \tag{B.9}
\]

\[
A_{y+} - A_{y-} = (\pi - \theta_y)r^2 + 2y\sqrt{r^2 - y^2} - 2ay
\]

\[
= (\pi - 2\cos^{-1}\frac{y}{r})r^2 + 2y\sqrt{r^2 - y^2} - 2ay \tag{B.10}
\]

When variations in \( \text{Sum} \) are small, \( (A_{x+} - A_{x-}) \) and \( (A_{y+} - A_{y-}) \) can be used to represent position information of the laser beam. A plot of \( \text{Sum} \) calculated from
Equation B.1 is shown in Figure B.2, and 
\((A_{x+} - A_{x-})\) and 
\((A_{y+} - A_{y-})\) calculated from Equation B.9 and B.10 in Figure B.3 and Figure B.4:

![Quadrant Photodiode Output: Sum](image)

**Figure B.2** Plot of \(\text{Sum}\) in Equation B.1

![Quadrant Photodiode Output: X (Y)](image)

**Figure B.3** Plots of \((A_{x+} - A_{x-})\) and 
\((A_{y+} - A_{y-})\)
Figure B.4 Plots of \((A_{x+} - A_{x-})/Sum\) and \((A_{y+} - A_{y-})/Sum\)
Appendix C

LABVIEW Data Acquisition

Data Acquisition is implemented through the following custom-written LabVIEW Virtual Instrument (VI) in LabVIEW® 2011. Figure C.1 shows the flow chart of the data acquisition process.

C.1 Signal Conditioning

The custom-made signal conditioning circuit box, Figure C.2, converts quadrant photodiode voltage outputs to the operational range of the LabJack U3-LV analog inputs. Channel A/B features a two stage operational amplifier circuit of which the first stage is a summing circuit to offset the bipolar signal to an unipolar signal and the second stage is a 1 to 1 voltage inverter to flip the negative signal to positive. Channel Sum is a single voltage divider to rescale the 12V QPD signal down to a 2.4V range.

Figure C.1 Data acquisition flow chart
Figure C.2 Signal conditioning circuit

Figure C.3 shows the characteristic curves of the circuits. Each channel operates in the linear regime during data acquisition. The linear fit parameters shown in Table C.1 acquired from the right figures are used in the LabVIEW Data Conversion Module in Figure C.7(b).
Figure C.3 Characteristic curves of channel A, B and Sum
The designed characteristics of the signal conditioning circuit is given below

\[ A(B)_{out} = \frac{1}{10}A(B)_{in} + 1.2V \]  \hspace{1cm} (C.1)

\[ Sum_{out} = \frac{1}{5}Sum_{in} \]  \hspace{1cm} (C.2)

### C.2 VI for LabJack U3-LV

The VI shown in Figure C.5 and Figure C.6, is designed to maintain independent control of two Uniblitz laser shutters during data acquisition. It consists of four parts: Shutter Control State Machine(Figure C.7(a)), Data Conversion Module(Figure C.7(b)), QPD Display Module, and File I/O Module.
Figure C.5 Front panel for All in One U3 Duo.vi
Figure C.6 Block diagram for All in One U3 Duo.vi
Figure C.7 All in One U3 Duo modules
Shutter Control is through a state machine shown in Figure C.7(a), consisting of various shutter mode combinations. The two shutters can operate individually or synchronized depending on the experiment. The direct voltage outputs of the quadrant photodiode are bipolar between ±12V which exceed LabJack U3-LV’s analog inputs’ unipolar range: 0 – 2.4V. Thus a custom-designed conversion circuit is used to bridge the quadrant photodiode outputs and LabJack inputs. The Data Conversion Module in LabVIEW software then converts the LabJack hardware inputs back into the true signal. The time-stamped data is stored in an ASCII file locally. The constant write access to the external ASCII file after data conversion imposes a noticeable overhead on data acquisition performance. Thus in real experiments, the raw data acquired from LabJack through the LabVIEW interface is passed on directly without data conversion to the write file. The data conversion is then completed through MATLAB programs during post-processing.

C.3 VI for LeCroy Oscilloscopes

The following VI’s, Figure C.9 - C.12, are written to retrieve real time waveform data from a LeCroy 9360 dual channel oscilloscope and a LeCroy LT372 dual channel oscilloscope in photoreorientation measurement. The oscilloscopes are connected to PC LabVIEW through GPIB488.2 interface. The time stamped data is then decimated by MATLAB programs before sent to Origin Pro. The flow chart for this process is shown in Figure C.8:

![Flow chart for photoreorientation data acquisition](image)

**Figure C.8** Flow chart for photoreorientation data acquisition
Figure C.9 Front panel for Read Scope LeCroy 9360 ii.vi
Figure C.10 Block diagram for Read Scope LeCroy 9360ii.vi
Figure C.11 Front panel for Read Scope LeCroy LT372i.vi
Figure C.12 Block diagram for Read Scope LeCroy LT372i.vi
Appendix D

Computer Scripts

D.1 Complete C Code for Numerical Simulation

Program main.c: main program file for heat transfer simulation.

Listing D.1 main.c

```c
#include "preamble.h"
#include "func,proto.h"

int main()
{
    Grid *g; // DATA DEFINITION
```
int m, n;  // DUMMY INDEX
int j;   // DUMMY INDEX
FILE * outht, * outnt, * outip;  // DATA FILE
FILE * sumtnt;  // DATA FILE

ALLOC_1D (g, 1, Grid);  // MEMORY ALLOCATION

outht= fopen("ht2","wb");  // OPEN TEMEPARATURE FILE
outnt= fopen("nt2","wb");  // OPEN NUMBER DENSITY FILE
outip= fopen("ip2","wb");  // OPEN INTENSITY FILE
sumtnt= fopen("tnt","wb");  // OPEN STRAIN FILE

gridInit (g);  // GRID INITIALIZATION
InitCond (g);  // INITIAL CONDITION
BondCond (g);  // BOUNDARY CONDITION

update2 (g);  // MAIN COMPUTATION
CalStrain(g);  // STRAIN COMPUTATION

/* STORE COMPUTATION RESULTS */

for (m=0;m<SizeX;m++){
    for (n=0;n<MaxTime;n++){
        fprintf (outht,"%g ", ht2 (m,n));
        fprintf (outnt,"%g ", nt2 (m,n));
        fprintf (outip,"%g ", ip2 (m,n));
    }
    fprintf (outht,"
");
for(j=0;j<MaxTime;j++) {
    fprintf(sumtnt,"%g %g\n", ntsumt(j), tsumt(j));
}

/* OBSERVATION POINT*/
printf("sizeof(g)=%d, MaxTime=%g(s), SizeX=%g(mm)\n",
    sizeof(Grid), MaxTime*(dt), SizeX*(dx)*1000);
printf("nt=%g, I=%g(W/m^2), T=%g(K)\n", nt2(10, MaxTime
    -100),ip2(10, MaxTime-100), ht2(10, MaxTime-100));
printf("nt=%g, I=%g(W/m^2), T=%g(K)\n", nt2(SizeX-10,
    MaxTime-100),ip2(SizeX-10, MaxTime-100), ht2(SizeX-10,
    MaxTime-100));

fclose(outht);           //CLOSE DATA FILE
fclose(outnt);           //CLOSE DATA FILE
fclose(outip);           //CLOSE DATA FILE
fclose(sumtnt);          //CLOSE DATA FILE
return 0;
}

Program gridsetup.c: initialize computation grid.
void gridInit(Grid *g) {
    MaxTime = num_time;
    SizeX = num_x;
    SizeY = num_x; // UNUSED FOR 1D
    SizeZ = num_x; // UNUSED FOR 1D
    dx = (20e-6); // 20um
    dt = (1e-3); // 1ms

    /* MEMORY ALLOCATION*/
    ALLOC_1D(g->ht, SizeX*MaxTime, double);
    ALLOC_1D(g->nt, SizeX*MaxTime, double);
    ALLOC_1D(g->nc, SizeX*MaxTime, double);
    ALLOC_1D(g->ipump, SizeX*MaxTime, double);
    ALLOC_1D(g->beta1, SizeX*MaxTime, double);
    ALLOC_1D(g->beta2, SizeX*MaxTime, double);
    ALLOC_1D(g->xi1, SizeX*MaxTime, double);
    ALLOC_1D(g->xi2, SizeX*MaxTime, double);
    ALLOC_1D(g->gamma, SizeX*MaxTime, double);
    ALLOC_1D(g->ntsum, MaxTime, double);
    ALLOC_1D(g->tsum, MaxTime, double);

    int i, j;
    for (i = 0; i < SizeX; i++)
        for (j = 0; j < MaxTime; j++) {
            bt12(i, j) = 0.2;  // BETA1
            bt22(i, j) = (1.0e4);  // BETA2
\[ xi12(i,j) = \left(1.0\times10^{-2}\right)/I0; \quad // QY1 \]

\[ xi22(i,j) = 0/I0; \quad // QY2 \]

```c
}
```

```c
}
```

/* boundary Condition*/

```c
void BondCond(Grid *g) {
    int j;
    for(j=0;j<MaxTime;j++) {
        ip2(0,j) = I0;
        ht2(0,j) = Ti + 2*qw/k*sqrt(alpha*j*dt/PI); \quad // b.c
        gm2(0,j) = a0*exp(-96600/8.413/(300 + ht2(0,j)));
    }
    return;
}
```

/* initial Condition*/

```c
void InitCond(Grid *g) {
    int i;
    for(i=0;i<SizeX;i++) {
        nt2(i,0) = 0.5;
        nc2(i,0) = 1 - nt2(i,0);
    }
    for(i=0;i<SizeX;i++) {
        ht2(i,0) = Ti;
        gm2(i,0) = a0*exp(-96600/8.413/(300 + ht2(i,0)));
    }
```
Program *update.c*: backbone of the computation.

**Listing D.3 update.c**

```c
#include "preamble.h"
#include "func-proto.h"

void update2(Grid *g) {
    int i=0, j=0;

    for(i=1;i<(SizeX);i++) {
        ip2(i,0) = ip2(i-1,0)-dx*bt22(i-1,0)*nt2(i-1,0)*ip2(i-1,0);
    }

    // ---------------Main ------------------
    for(j=0;j<(MaxTime-1);j++) {
        for(i=1;i<(SizeX-1);i++) {
            nt2(i-1,j+1) = nt2(i-1,j)+dt*(-xi12(i-1,j)*ip2(i-1,j)*nt2(i-1,j)+xi22(i-1,j)*ip2(i-1,j)*nc2(i-1,j)+gm2(i-1,j)*nc2(i-1,j));
            nc2(i-1,j+1) = 1.0-nt2(i-1,j+1);
            gm2(i,j+1) = a0*exp(-96600/8.413/(300+ht2(i,j)));
            ht2(i,j+1) = ht2(i,j)+P*(dt/(dx*dx))*(ht2(i+1,j)-2*ht2(i,j)+ht2(i-1,j))+dt*P/k*bt12(i,j)*ip2(i,j)*nt2(i,j);
        }
    }
}
```
\[ \text{ip2}(i,j+1) = \text{ip2}(i-1,j+1) - dx \cdot bt22(i-1,j+1) \cdot nt2(i-1,j+1) \cdot \text{ip2}(i-1,j+1); \]

\[
\}
\]

//THE REMAINING BOUNDARY CONDITIONS FOR NT, HT, AND I

\[ \text{ht2}(\text{SizeX}-1,j+1) = 1/(1+h*\text{dx}/k)*(\text{ht2}(\text{SizeX}-2,j+1)+h*\text{dx}/k*Te); //B.c.2 \]

\[ \text{ip2}(\text{SizeX}-1,j+1) = \text{ip2}(\text{SizeX}-2,j+1) - dx*bt22(\text{SizeX}-2,j+1)*nt2(\text{SizeX}-2,j+1)*\text{ip2}(\text{SizeX}-2,j+1); \]

\[ \text{nt2}(\text{SizeX}-2,j+1) = \text{nt2}(\text{SizeX}-2,j)+dt*(-xi12(\text{SizeX}-2,j)*\text{ip2}(\text{SizeX}-2,j)*nt2(\text{SizeX}-2,j)+xi22(\text{SizeX}-2,j)*\text{ip2}(\text{SizeX}-2,j)*nc2(\text{SizeX}-2,j)+gm2(\text{SizeX}-2,j)*nc2(\text{SizeX}-2,j)); \]

\[ \text{nc2}(\text{SizeX}-2,j+1) = 1.0-nt2(\text{SizeX}-2,j+1); \]

\[ \text{nt2}(\text{SizeX}-1,j+1) = \text{nt2}(\text{SizeX}-1,j)+dt*(-xi12(\text{SizeX}-1,j)*\text{ip2}(\text{SizeX}-1,j)*nt2(\text{SizeX}-1,j)+xi22(\text{SizeX}-1,j)*\text{ip2}(\text{SizeX}-1,j)*nc2(\text{SizeX}-1,j)+gm2(\text{SizeX}-1,j)*nc2(\text{SizeX}-1,j)); \]

\[ \text{nc2}(\text{SizeX}-1,j+1) = 1.0-nt2(\text{SizeX}-1,j+1); \]

\[ \text{gm2}(\text{SizeX}-1,j+1) = a0*exp(-96600/8.413/(300+\text{ht2}(\text{SizeX}-1,j))); \]

\[
\}
\]

return;

\}

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{ 
  ntsumt(j) = 0.0;
  for(i=0;i<SizeX-1;i++){
    ntsumt(j) = ntsumt(j)+((2*nt2(i,j)-1.0)/1.0)*dx; //
    
    \begin{center}
    \textbf{Elongation due to Trans-cis Isomerization}
    \end{center}
  }
}

for(j=0;j<MaxTime;j++){
  tsumt(j) = 0.0;
  for(i=0;i<SizeX-1;i++){
    tsumt(j) = tsumt(j)+(ht2(i+1,j)+ht2(i,j))/2*dx; //
    
    \begin{center}
    \textbf{Elongation due to Temperature Increase}
    \end{center}
  }

  return;
}

Program \texttt{ht_grid.h}: header file for grid structure definition.

\textbf{Listing D.4 ht-grid.h}

\begin{verbatim}
# ifndef _HT_GRID_H
#define _HT_GRID_H
/* GRID DEFINITION*/
enum GRIDTYPE {oneDGrid, twoDGrid, threeDGrid};

struct Grid {
  double *ht, *nt, *nc, *ipump;
  double *ntsum, *tsum;
  double *beta1,*beta2,*xi1,*xi2,*gamma;
  int sizeX, sizeY, sizeZ;
\end{verbatim}
int time, MaxTime;
int type;
double dX, dT;
}

typedef struct Grid Grid;

Program parameter.h: header file for parameter definition.

Listing D.5 parameter.h

```c
#ifndef _PARAMETER_H
#define _PARAMETER_H

///////////Define Parameters///////////

// k = thermal conductivity
#define PI (3.1415926)

// alpha = thermal diffusivity
#define num_x (250) // 250 x 20um = 5 mm
#define num_time (10000) // 1E4 x 1ms = 10 s
#define Ti 0.0 // initial fiber temperature
#define Te 0.0 // environment temperature
#define alpha (1.5e-7) // m^-2/s
#define k 0.2 // 0.167 - 0.25 W/m K (PMMA)
#define I0 (5.0e4) // 5.0e4 W/m^2
#define qw (0.2*I0) // 1.0e3
#define h (1.0e4) // heat transfer coefficient
#define a0 (7.5e12) // max thermal rate
#define P alpha

#define PI (3.1415926)
```

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Program **func_proto.h**: header file for function declaration.

---

**Listing D.6** func-proto.h

```c
#ifndef _FUNCPROTO_H
#define _FUNCPROTO_H

/* Function declaration*/
#include "preamble.h"

void gridInit(Grid *g); //GRID INITIALIZATION
void update2(Grid *g);  //UPDATE COUPLED
void InitCond(Grid *g); //INITIAL CONDITION
void BondCond(Grid *g); //BOUNDARY CONDITION
void CalStrain(Grid *g); //CALCULATE STRAIN
#endif
```

Program **preamble.h**: header file to convert 3D arrays into 1D pointers.

---

**Listing D.7** preamble.h

```c
#ifndef _PREAMBLE_H
#define _PREAMBLE_H

#pragma once

// //////////Include ///////////
#include <stdlib.h> //STANDARD LIB HEADER
#include <stdio.h>
#include <complex.h>
#include <math.h>
#include "ht-grid.h" //CUSTOM HEADER
#include "parameter.h"
#include "fdtd-alloc.h"

// //////////DEFINE MACROS///////////
```
/* Specify elements of structure "G"*/
/* e.g., SizeX = num_row, SizeY = num_column*/
/* e.g., Ez(M, N, P) => ez[((M) * num_columns + (N)) * num_rows + (P)]*/

#define Ht1G(G, M) G->ht[(M)]
#define Ht2G(G, M, T) G->ht[(M)*(MaxTime) + (T)]
#define Nt1G(G, M) G->nt[(M)]
#define Nt2G(G, M, T) G->nt[(M)*(MaxTime) + (T)]
#define Nc1G(G, M) G->nc[(M)]
#define Nc2G(G, M, T) G->nc[(M)*(MaxTime) + (T)]
#define Ip1G(G, M) G->ipump[(M)]
#define Ip2G(G, M, T) G->ipump[(M)*(MaxTime) + (T)]
#define Bt11G(G, M) G->beta1[(M)]
#define Bt12G(G, M, T) G->beta1[(M)*(MaxTime) + (T)]
#define Bt21G(G, M) G->beta2[(M)]
#define Bt22G(G, M, T) G->beta2[(M)*(MaxTime) + (T)]
#define Xi11G(G, M) G->xi1[(M)]
#define Xi12G(G, M, T) G->xi1[(M)*(MaxTime) + (T)]
#define Xi21G(G, M) G->xi2[(M)]
#define Xi22G(G, M, T) G->xi2[(M)*(MaxTime) + (T)]
#define Gm1G(G, M) G->gamma[(M)]
#define Gm2G(G, M, T) G->gamma[(M)*(MaxTime) + (T)]
#define NtSum1G (G, M) G->ntsum[(M)]
#define Tsum1G (G, M) G->tsum[(M)]

/* Specify elements of structure "g"*/

#define ht1 (M) Ht1G(g, M)
#define nt1 (M) Nt1G(g, M)
#define nc1(M) Nc1G(g, M)
#define ip1(M) Ip1G(g, M)
#define bt11(M) Bt11G(g, M)
#define bt21(M) Bt21G(g, M)
#define xi11(M) Xi11G(g, M)
#define xi21(M) Xi21G(g, M)
#define gm1(M) Gm1G(g, M)
#define ntsumt(M) NtSum1G(g, M)
#define tsumt(M) Tsum1G(g, M)
#define ht2(M, T) Ht2G(g, M, T)
#define nt2(M, T) Nt2G(g, M, T)
#define nc2(M, T) Nc2G(g, M, T)
#define ip2(M, T) Ip2G(g, M, T)
#define bt12(M, T) Bt12G(g, M, T)
#define bt22(M, T) Bt22G(g, M, T)
#define xi12(M, T) Xi12G(g, M, T)
#define xi22(M, T) Xi22G(g, M, T)
#define gm2(M, T) Gm2G(g, M, T)

/* Specify miscellaneous parameters*/
#define SizeXG(G) G->sizeX
#define SizeYG(G) G->sizeY
#define SizeZG(G) G->sizeZ
#define SizeX SizeXG(g)
#define SizeY SizeYG(g)
#define SizeZ SizeZG(g)
#define TimeG(G) G->time
#define MaxTimeG(G) G->MaxTime
Program `fdtd_alloc.h`: header file to define memory allocation macros[56].

Listing D.8 fdtd-alloc.h
if(!PNTR){
    perror("ALLOC_2D");
    fprintf(stderr,
        "Allocation failed for ", PNTR", terminating...
    exit(-1);
}
#
define ALLOC_3D(PNTR, NUMX, NUMY, NUMZ, TYPE)
    PNTR = (TYPE*) calloc((NUMX)*(NUMY)*(NUMZ), sizeof(TYPE));
    if(!PNTR){
        perror("ALLOC_3D");
        fprintf(stderr, "Allocation failed for ", PNTR", terminating...
        exit(-1);
    }
#endif

D.2 MATLAB Code for Data Plot

Program htfem_load.m: load C computed data files into MATLAB.

Listing D.9 htfem_load.m

1 %LOAD ASCII DATA
2 close all;clear all;clc;
3 tic;
4 s1 = load('ip2');  % PUMP INTENSITY
5 toc

1By courtesy of Professor John B. Schneider, EECS, Washington State University
6    s2 = load('nt2'); \% Population density of trans
7    toc
8    s3 = load('ht2'); \% Temperature
9    toc

Program htfem_mesh_hd.m: 3D plot of computation results from C.

Listing D.10 htfem_mesh_hd.m

1    htfem_load;
2        ns = size(s1);
3        mx = ns(1); \% SPACE DIMENSION = 250
4        nx = ns(2); \% TIME STEP = 10000
5        s1 = s1'; s2 = s2'; s3 = s3';
6    figure(1);
7        [X,Y]=meshgrid(1:mx,1:nx);
8       h=surf(X,Y,s1);
9       set(h,'LineStyle','none');
10      xlabel('X'); ylabel('Time'); zlabel('I');
11      title('Intensity');
12
13    figure(2);
14        [X,Y]=meshgrid(1:mx,1:nx);
15       h=surf(X,Y,s2);
16       set(h,'LineStyle','none');
17      xlabel('X'); ylabel('Time'); zlabel('N-Trans');
18      title('Number density of trans');
19
20    figure(3);
21
Program \texttt{htfem\_2d.m}: plot section view of space and time evolution data.

\begin{verbatim}
Listing D.11 htfem\_2d.m

1 htfem_load;
2   ns = size(s1);
3   mx = ns(1); \% SPACE DIMENSION = 250
4   nx = ns(2); \% TIME STEP = 10000
5 figure(1); \%\%\%---Plot evolution over space---\%\%\%
6 for n=1:nx
7     if mod(n,100)==1
8         subplot(3,1,1);
9         plot(s1(:,n));xlabel('x');ylabel('I');
10        title('Intensity');
11        axis([1 mx 0 1e5]);\%IPUMP
12        hold on;
13
14         subplot(3,1,2);
15         plot(s2(:,n));xlabel('x');ylabel('N-trans');
16         title('Number density of trans isomer');
17         axis([1 mx 0 1]);\%IPUMP
18         hold on;
19
20         subplot(3,1,3);
21         plot(s3(:,n));xlabel('x');ylabel('T');
22         title('Temperature');
\end{verbatim}

21      axis([1 mx 0 80]); % IPUMP
22      hold on;
23      pause(0.2);
24      Time_Stamp = n
25      end
26      end
27
28      s1 = s1'; s2 = s2'; s3 = s3';
29      figure(2); %%% --- PLOT EVOLUTION OVER TIME --- %%%
30      for m =1:mx
31            if mod(m,5)==1
32                subplot(3,1,1);
33                plot(s1(:,m));xlabel('Time');ylabel('I');
34                title('Intensity');
35                axis([1nx 0 1e5]); % IPUMP
36                hold on;
37                subplot(3,1,2);
38                plot(s2(:,m));xlabel('Time');ylabel('N-trans');
39                title('Number density of trans isomer');
40                axis([1nx 0 1]); % NT
41                hold on;
42                subplot(3,1,3);
43                plot(s3(:,m));xlabel('Time');ylabel('T');
44                title('Temperature');
45                axis([1nx 0 80]); % NT
46                hold on;
47                pause(0.2);
Program htfem_strain.m: plot strain.

Listing D.12 htfem_strain.m

close all; clear all; clc;
s=load('tnt');

a=1.0e-2; \texttt{\%TEMPERATURE}
b=6.785e-1; \texttt{\%PHOTOISOMERIZATION}
c=a*s(:,2) + b*s(:,1);
d=2*c./(1-c.^2);

subplot(1,3,1);
  plot(b*s(:,1));
  xlabel('Time(ms)');
  ylabel('Isomerization contribution');

subplot(1,3,2);
  plot(a*s(:,2));
  xlabel('Time(ms)');
  ylabel('Temperature contribution');

subplot(1,3,3);
  plot(c);
  xlabel('Time(ms)');
  ylabel('Elongation');
D.3 MATLAB Code for LabJack Data Conversion

Program **runitall2.m**: convert all data files in a folder directory.

---

**Listing D.13 runitall2.m**

```matlab
1 %RUNITALL2.M
2 %LOAD AND CONVERT ALL FILES IN A FOLDER
3 %ADVANCED VERSION OF "RUNITALL.M"
4 %AUTHOR: XIANJUN YE
5 myFolder = 'D:\Work\Dropbox\MATLAB\data\2013042301';
6 if ~isdir(myFolder)
7    errorMessage = sprintf('Error: Folder Not Found:
6                        myFolder);
8    uiwait(warndlg(errorMessage));
9    return;
10 end
11 % clf;
12 filePattern = fullfile(myFolder, '*.txt'); % BUILD FULL
13     FILENAME OF THE DIR
14 txtFiles = dir(filePattern); % LIST CONTENTS OF THE FOLDER
15 m = 0;
16 mm = [1 10 20];
17 % BUILD CELL ARRAY
18 for k = 1:length(txtFiles)
19    baseFileName = txtFiles(k).name;
20    fullfile = fullfile(myFolder, baseFileName);
21    %PRINTF(1, 'NOW READING %s\n', fullfile);
22    myData{k} = load(fullfile);
```
s = myData{k};

[path name ext] = fileparts(fullFileName); % STRIP FILENAME

tprfx = transpose(strread(name, ’%c’, 15));

for nn = mm

% Avg2DS(s, NN, TPRFX);
RMS2DS(s, nn, tprfx);
end

% SELECT DATA FILES TO CONVERT BY SIZE
%
if txtFiles(k).bytes<60000

smv = mvavg1d(myData{k}(:,3),100,0); % y(:,3), x(:,2)
plot(smv, ’o’)
axis([0 1100 1.2 1.225]); % y scale
%axis([0 1000 1.225 1.24]); % x scale
hold on;
m = m + 1

end

}%

fprintf(’Done Reading %s
’, baseFileName);

%pause(.5);
end

Program RMS2DS.m: function definition to calculate RMS of 2D data.

Listing D.14 RMS2DS.m

function [outmx2d] = RMS2DS(s, n, fprefix)
% Calculate the root mean square of every n points from
original 2D data.
% This is not a moving averaging method.
% Written on 12/23/2011
% Omit file loading process, saving time
% s = input data array
% n = number of points to average
% fprefix = prefix string added to output file name

tic
szs = size(s);
p = floor(szs(1)/n);
m = szs(2);
outmx2d = zeros(p,m);

for k = 1:m
    outmx2d(:,k) = RMS1D(s(:,k), n, 0);
end

if nargin < 3, fprefix = datestr(now, 'yyyymmdd_HHMMSS'); end
fid2 = strcat(fprefix,'_',num2str(n),'_','outrms','_.txt');
save(fid2, 'outmx2d', '-ascii');
toc

Program Avg2DS.m: function definition to calculate average of 2D data.
% Averaging every n points from original 2D data.
% This is not a moving averaging method.
% Written on 12/20/2011
% Omit file loading process, saving time
% s = input data array
% n = number of points to average
% fprefix = prefix string added to output file name

tic
szs = size(s);
p = floor(szs(1)/n);
m = szs(2);
outmx2d = zeros(p,m);

for k = 1:m
    outmx2d(:,k) = Avg1D(s(:,k), n, 0);
end

outmx2d(:,1) = outmx2d(:,1)*5.20772 - 0.062;
outmx2d(:,2) = outmx2d(:,2)*9.95604 - 12.27078;
outmx2d(:,3) = outmx2d(:,3)*9.95757 - 12.15328;

if nargin < 3, fprefix = datestr(now, 'yyyyymmdd_HHmmss'); end
fid2 = strcat(fprefix, '_', num2str(m), '_', 'out', '.txt');
save(fid2, 'outmx2d', '-ascii');
toc

Program **RMS1D.m**: function definition to calculate RMS of 1D data.

---

**Listing D.16 RMS1D.m**

140
function [outmx] = RMS1D(inmx, n, sflg)

% Calculate the root mean square of every n points from original 1D data.

% This is not a moving averaging method.
% Written on 12/23/2011

% inmx = input array
% n = number of points to average
% sflg = 1: save to file
% else : don’t save

mnmx = mean(inmx,1);
szmx = size(inmx);
m = floor(szmx(1)/n);
rmmx = szmx(1) - m*n;

for k = 1:m
    outmx(k) = sqrt(mean(inmx((k*n-n+1):k*n).^2));
end
outmx = transpose(outmx);

% Save to File
if sflg == 1
    t1 = datestr(now, 'yyymmd_HHMSS');
    fid = strcat(t1, '_', 'rms', '.txt');
    save(fid, 'outmx', '-ASCII');
    fid
end

[szmx(1), n, m, rmmx, mnmx]

Program Avg1D.m: function definition to calculate average of 1D data.
Listing D.17 Avg1D.m

function [outmx] = Avg1D(inmx, n, sflg)

% AVERAGING EVERY N POINTS FROM ORIGINAL 1D DATA.
% THIS IS NOT A MOVING AVERAGING METHOD.
% WRITTEN ON 12/20/2011
% INMX = INPUT ARRAY
% N = NUMBER OF POINTS TO AVERAGE
% SFLG = 1: SAVE TO FILE
% ELSE: DON’T SAVE

mnmx = mean(inmx,1);

szmx = size(inmx);

m = floor(szmx(1)/n);
rmmx = szmx(1) - m*n;

for k = 1:m
    outmx(k) = mean(inmx((k*n-n+1):k*n));
end

outmx = transpose(outmx);

% SAVE TO FILE
if sflg == 1
    t1 = datestr(now, 'yyyymmdd_HHMMSS');
    fid = strcat(t1, '_', 'outmx', '.txt');
    save(fid, 'outmx', '-ASCII');
    fid
end

[szmx(1) n m rmmx mnmx]
D.4 MATLAB Code for Image Processing

Program FrameOut.m: extract frames from a video file.

Listing D.18 FrameOut.m

```
1 % THIS SCRIPT IS INTENDED TO EXTRACT FRAMES ... 
2 % FROM VIDEO FILE IN A STRUCTURED MANNER. 
3 % WRITTEN ON 7/25/2011 
4 close all; clc; 
5 % READ VIDEO FILE 
6 obj = 'f:\DATAII\My Movie.wmv'; 
7 % VIDEO FORMAT: *.wmv, *.mp4,... 
8 mov = VideoReader(obj); 
9 info = get(mov); 
10 %---------- VIDEO INFORMATION ----------- 
11 %%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
12 % INFO = Duration: 3.1249e+004 % 
13 % Name: 'My Movie.wmv' % 
14 % Path: 'F:\DATAII' % 
15 % Tag: '' % 
16 % Type: 'VideoReader' % 
17 % UserData: [] % 
18 % BitsPerPixel: 24 % 
19 % FrameRate: 29.9700 % 
20 % Height: 240 % 
21 % NumberOfFrames: [] %936541% % 
22 % VideoFormat: 'RGB24' % 
23 % Width: 426 % 
```
lastFrame = read(mov,inf);
nFrames = mov.NumberOfFrames;
vidHeight = mov.Height;
vidWidth = mov.Width;

% OUTPUT ONE FRAME EVERY 'nFrameInc' FRAMES.
nFrameInc = 300;

% CREATE FOLDER TO STORE EXTRACTED FRAMES
mkdir('F:\DATAII\Frames\002\');
a1='F:\DATAII\Frames\002\Frame_';
for m = 1:nFrames
    im1 = read(mov, m);
    % ADD ZERO TO FRAME NAME
    a2 = add02StrN(nFrames, m);
    % CONSTRUCT FRAME FILENAME
    b1 = [a1 a2 '.jpeg'];
    % SAVE EXTRACTED FRAME TO FILE
    if mod(m, nFrameInc) == 0
        imwrite(im1,b1,'jpeg');
    end
end

% PLAY NEWLY EXTRACTED FRAMES
msrow(0.5);

Program add02StrN.m: function definition to add leading zeros to filenames.

Listing D.19 add02StrN.m
function stradd = add02StrN( nFrames, nimg )

% Add leading zeros in front of the image number whenever its
% digits is shorter than the total digits of max image number.
% Written on 7/25/2011, Xianjun

% nFrames = 936541;
% nimg = 130;

nn = floor(log10(nFrames)) + 1;
strk = num2str(nimg);
kk = floor(log10(nimg)) + 1;
mm = nn - kk;
for pp = 1:mm
    b = strcat('0', strk);
    strk = b;
end
stradd = strk;

% Returns a string
Bibliography


