ARL-SR-0434 ● FEB 2021

2020 DEVCOM Army Research Laboratory Summer Student Program, Volume I: Symposium Presentations

Compiled by Danell Diggs

Approved for public release; distribution is unlimited.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

ARL-SR-0434 ● FEB 2021



2020 DEVCOM Army Research Laboratory Summer Student Program, Volume I: Symposium Presentations

Compiled by Danell Diggs
Outreach Office, Plans and Programs, Laboratory Operations,
DEVCOM Army Research Laboratory

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.
PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
February 2021	Special Report	2020

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
2020 DEVCOM Army Research Laboratory Summer Student Program, Volume I: Symposium Presentations	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)	5d. PROJECT NUMBER
Compiled by Danell Diggs	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
DEVCOM Army Research Laboratory ATTN: FCDD-RLL-D 2800 Powder Mill Rd Adelphi, MD 20783-1138	ARL-SR-0434

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

The US Army Combat Capabilities Development Command Army Research Laboratory Summer Student Symposium is a DEVCOM Army Research Laboratory Director's Award Program for all the students participating in various summer scholarship and contract activities across ARL. The goal of the program is to recognize and publicize exceptional achievements made by students and their mentors in support of Army science. All undergraduate and graduate interns were encouraged to submit an abstract summarizing their accomplishments and participate in the symposium. Presentations given by all directorate finalists are published in Volume I of the proceedings (this report), while abstracts are collected in Volume II ("Compendium of Abstracts"; ARL-SR-0435).

15. SUBJECT TERMS

DEVCOM ARL Summer Student Research, Summer Student Symposium, Student Outreach

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Danell Diggs
Unclassified	Unclassified	Unclassified	UU	98	19b. TELEPHONE NUMBER (Include area code) (301) 394-1092

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

Director's Foreword **iv**

1. Introduction **1**

2. 2020 ARL Summer Student Symposium **2**

2.1 Undergraduate Category Winners 2

2.2 Graduate Category Winners 2

3. Undergraduate Presentations **3**

4. Graduate Presentations **59**

Distribution List **92**

Director's Foreword

The US Army Combat Capabilities Development Command Army Research Laboratory mission is to "operationalize science for transformational overmatch". As the Army's corporate research laboratory, we provide the technological underpinnings critical to providing capabilities required by the future Army.

In the coming years, our nation is projected to experience a shortage of scientists and engineers. Our laboratory recognizes the criticality of intellectual capital in generating future capabilities for the Army. It is critically important that we address the projected shortfall and make it a key responsibility of ours to close the impending gap. We have, therefore, identified the nation's next generation of scientists and engineers as a key community of interest, and have generated a robust educational outreach program to strengthen and support them. We have achieved many successes with this community. We believe that the breadth and depth of our outreach programs will have a significant and positive effect on the participants, facilitating their journey toward becoming our nation's next generation of scientists and engineers.

A fundamental component of our outreach program is to provide students research experiences at the DEVCOM Army Research Laboratory. During the summer of 2020, we supported research experiences at ARL for over 180 undergraduate and graduate students. Due to the COVID-19 pandemic, we were able to adapt and provide a highly effective virtual experience. As part of their experience, students present the results of the work they performed while at ARL. All of the presentation were of high quality, but only a few could be presented at our student symposium. The finalist presentations prepared this summer are contained in this volume of the proceedings, and they indicate that there were many excellent research projects with outstanding results. It is unfortunate that there was not enough time for us to have all of the presentation presented. We would have enjoyed hearing them all.

We are very pleased to have hosted this outstanding group of students for the summer. It is our hope that they will continue their pursuit of technical degrees and will someday assist us in providing critical scientific outcomes for our Army.

Patrick Baker
Director

1. Introduction

The US Army Combat Capabilities Development Command Army Research Laboratory Summer Student Symposium is a DEVCOM Army Research Laboratory Director's Award Program for students participating in various summer internship opportunities across ARL. The goal of the program is to recognize and publicize exceptional achievements made by the students and their mentors in the support of Army science.

All undergraduate and graduate interns are eligible to compete for a finalist position and give an oral presentation at the symposium. All students, including high school students in the Science and Engineering Apprentice Program (SEAP), are encouraged to present posters at the symposium and submit abstracts summarizing their accomplishments.

Oral presentations at the symposium are given by finalists selected based on directorate-level competitions. Each directorate can send one graduate student and one undergraduate finalist to the symposium.

This year's symposium was held at the Mallette Center at Aberdeen Proving Ground, Maryland, on Thursday, 6 August 2020. Oral presentations were judged by a panel of senior ARL scientists (including ARL Fellows and Chief Scientists). Students with the top three presentations ("Corporate Medalists") were awarded the ARL Summer Student Research Gold ($500), Silver ($300), and Bronze ($200) awards in the undergraduate and graduate student levels.

This volume of the Summer Student Symposium Proceedings contains presentations given by all directorate finalists at the symposium. Volume II (ARL-SR-0435) is a compendium of student abstracts.

2. 2020 ARL Summer Student Symposium

2.1 Undergraduate Category Winners

Gold Medalist:

Bryson Howell, Computation and Information Sciences Directorate

Classification of Predatory Behaviors in Multi-Agent Systems

Silver Medalist:

Jenille Cruz, Sensors and Electron Devices Directorate

Atomistic Probing of Catalytic Activities in H and O-Terminated Diamond (100) Surfaces

Bronze Medalist:

Jaclyn McLaughlin, Weapons & Materials Research Directorate

Development of a Toughened Thermoset Vinyl Ester Photolithography Resin for High-Performance Additive Manufacturing (AM)

2.2 Graduate Category Winners

Gold Medalist:

Peter Ryseck, Vehicle Test Directorate

Quadrotor Biplane: Wind Tunnel Setup and Flight Testing

Silver Medalist:

Erick Guzman, Sensors and Electron Devices Directorate

Study of Thermal and Vibrational Properties of Terminated Diamond Surfaces from First Principle Calculations

Bronze Medalist:

Ben Evangelisti, Weapons and Materials Research Directorate

Understanding the Effects of Carbon-Coating on the Oxidation of Aluminum Nanoparticle Using Molecular Dynamics Simulations

3. Undergraduate Presentations

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Identification of Collaborative Behaviors in Multi-Agent Systems

The University of Tennessee, Knoxville
Bryson Howell
Mentor: Erin Zaroukian, CISD-ISD-CUB
Computer Scientist

Distribution Unlimited

06 AUG 2020

UNCLASSIFIED

MOTIVATION

- **Multi-Agent Reinforcement Learning (MARL)**
  - Form of machine learning
  - Deep RL has been proven to allow agents to perform complex cooperative tasks [1]
  - Teams can be homogeneous or heterogeneous
  - Heterogeneous strategies tend to perform better than homogeneous ones [2]
- **Classification of Behavior**
  - Hard to say if heterogeneous agents are truly collaborating
  - Need a way to measure collaboration



Coordination – an explicit relationship between actors that is described by directly observable quantities.
- e.g., perfectly synchronized dancing agents

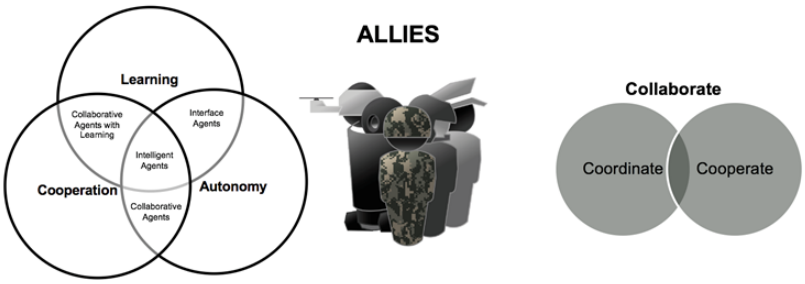
Cooperation – an implicit relationship between actors that is described by inference associated with a common goal.
- e.g., baking a cake and cooking a steak (independent sub-goals)

Collaboration - the intersection of both coordination and cooperation.
- e.g., pursuer agents working together to capture an evader agent

[1] A. Tampuu, T. Matiisen, D. Kodelja, I. Kuzovkin, K. Korjus, J. Aru, et al., "Multiagent cooperation and competition with deep reinforcement learning," *PLoS ONE*, vol. 12, no. 4, 2017.
[2] R. Fernandez, E. Zaroukian, J. D. Humann, B. Perelman, M. R. Dorothy, S. S. Rodriguez, and D. E. Asher, "Emergent heterogeneous strategies from homogenous capabilities in multi-agent systems," Internal work-in-progress 2020.

OBJECTIVE

- **Identify collaborative heterogeneous strategies that are emergent from MARL systems**

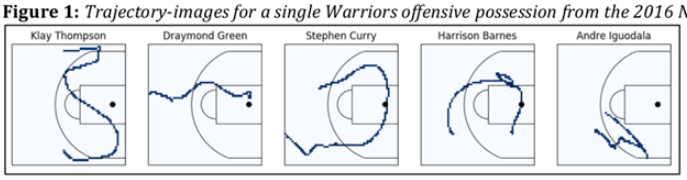


RELATED WORK

- **Human Teams**
  - [3] Clustered trajectory images of NBA players' movements
  - Assigned "profiles" to different players describing their individual offensive strategy
  - According to [4], the strategy of a team can be analyzed through metrics describing the team's formation

- **MARL Teams**
  - Group dynamics of MARL system were estimated using techniques from graph theory [5]

Figure 1: *Trajectory-images for a single Warriors offensive possession from the 2016 NBA Finals*



[3] A. Nistala and J. Guttag, "Using deep learning to understand patterns of player movement in the NBA," *Proceedings of the MIT Sloan Sports Analytics Conference*, 2019.
[4] A. Santiago, B. Calder, and K. Gemp, "Leveraging advances in spatial-temporal analytics for use in mission performance analysis," MITRE Corporation, Tech. Report. 18-4197. Dec. 2018.
[5] E. Zaroukian, S. S. Rodriguez, S. L. Barton, J. Schaffer, B. Perelman, N. R. Waytowich, et al. "Algorithmically identifying strategies in multi-agent game-theoretic environments", In SPIE Defense + Commercial Sensing, 2019.

METHODS

- **Environment**
  - 2D particle environment using OpenAI's Gym library
  - Predator-Prey pursuit task [6]
    - 3 physically homogeneous predator agents must chase a prey agent
    - Prey agent is ~30% smaller and faster than the predator agents
- **MADDPG Algorithm**
  - Agents are trained with a centralized critic
  - After training, agents remain decentralized [6]
  - Predators are equally rewarded when one of them collides with the prey agent
  - The prey agent receives the opposite reward
- **Experiment Process**
  - Models are trained in the pursuit task for 100,000 episodes
  - Learning is then disabled, and agent behavioral data is collected from 1000 episodes of the task
  - Experiment is repeated for homogeneous teams

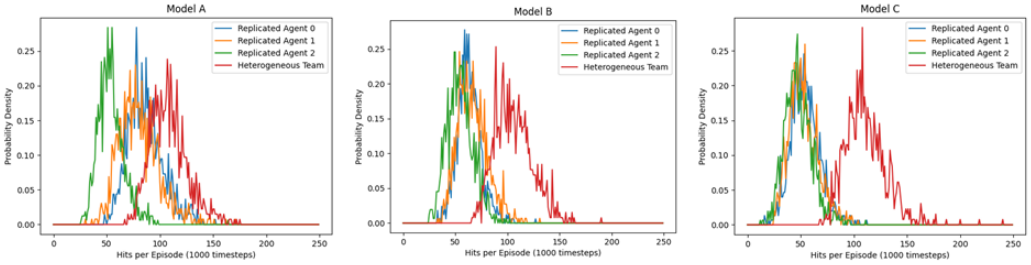


[6] R. Lowe, Y. I. Wu, A. Tamar, J. Harb, O. P. Abbeel, and I. Mordatch, "Multi-agent actor-critic for mixed cooperative-competitive environments," in *Advances in neural information processing systems*, 2017, pp. 6379-6390.

UNCLASSIFIED

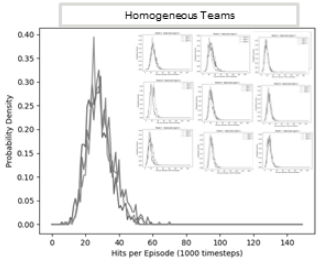
RESULTS

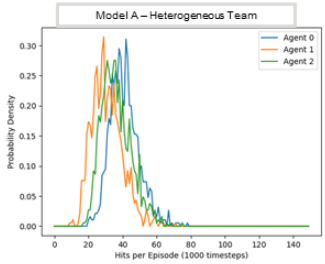
- **Points Scored on the Prey**
  - Representative of overall team performance
  - The heterogeneous team outperforms the homogeneous teams in all cases, confirming prior work.
  - Heterogeneous team performance is similar across all models
  - Homogeneous team performance is more variable

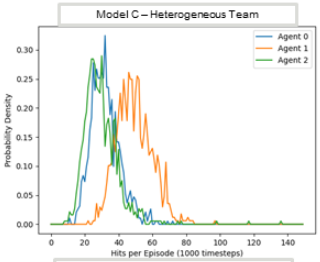


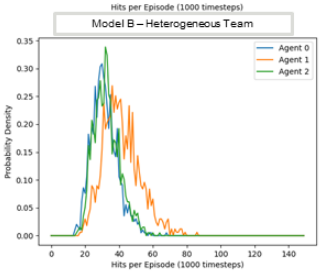
RESULTS

- **Points Scored by Individual Predators**
  - Could give insight into strategy being used by each agent
    - E.g. "Chaser" agents and "Interceptor" agents
  - Differs from model to model for heterogeneous teams
  - Homogeneous teams showed no great variation in performance



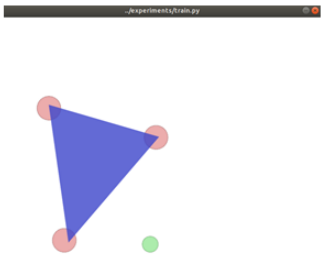


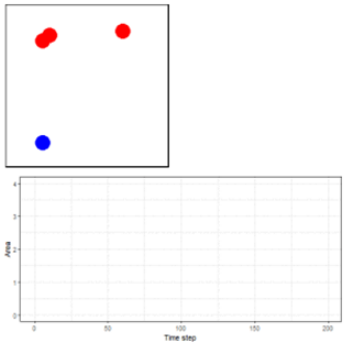




RESULTS

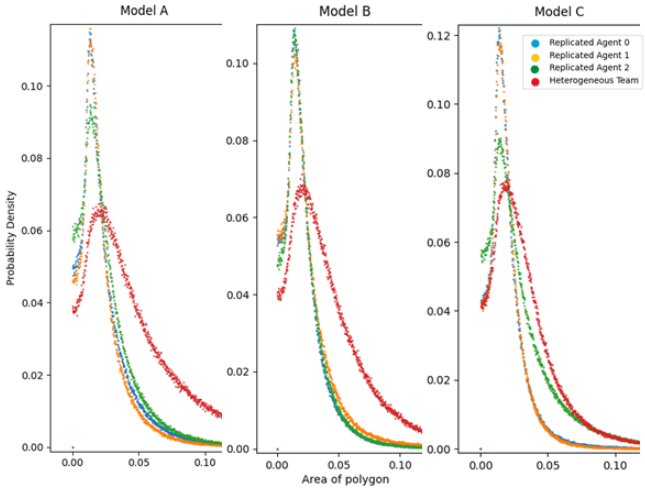
- **Predator Polygon Area**
  - Area of polygon formed by connecting all the predator agents
  - Measures the team's spatial distribution
  - Can give insight into collaborative strategies





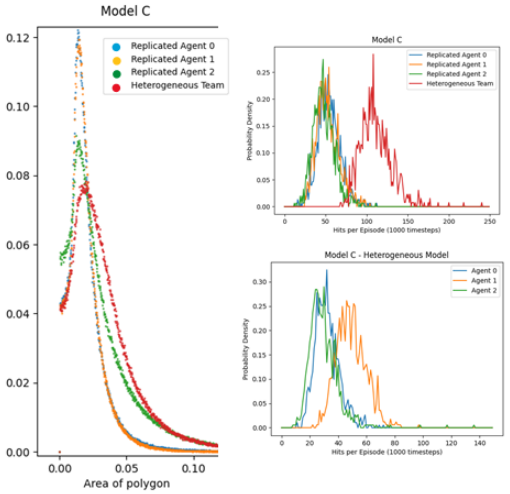
PREDATOR POLYGON AREA

- **Observations**
  - All area probabilities appear to have a logarithmic distribution
  - Heterogeneous team area varied slightly across all models
  - Homogeneous team area varies more strongly
  - This variation reinforces that the heterogeneous agents are using different and potentially complementary policies



DISCUSSION

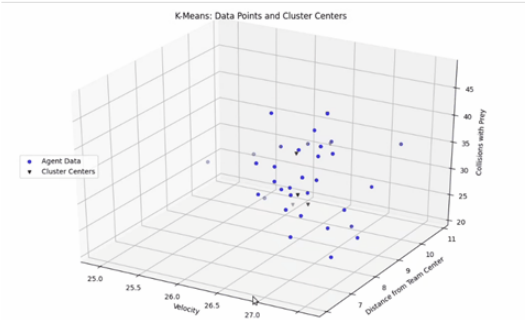
- **Is Polygon Area Related to Performance?**
  - Heterogeneous teams score high and are more distributed spatially
  - The same trend does not appear for homogeneous teams
- **How Can We Measure Collaboration?**
  - Performance alone is not enough, we need a combination of factors
  - The variation in individual agent and homogeneous team behavioral metrics indicates that agents are learning unique policies
  - Uneven individual performances could indicate that agents are developing weaker individual policies to help the team as a whole
  - We have qualitative results hinting at collaboration, but we need to perform more analysis



FUTURE WORK

- **Cluster Analysis**
  - We want to classify the behavior of individual agents
  - K-means clustering using the behavioral metrics of each agent can quantitatively show how the strategies they use differ
  - Ideally, we will be able to place agents in a relatively small number of clusters

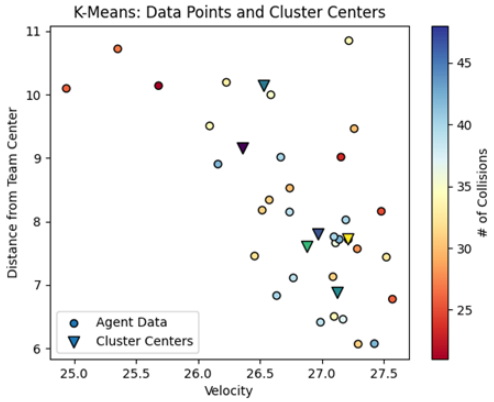
- **Creating New Teams**
  - Identifying which individual agents are using similar strategies will give us insight into team structure
  - It would be interesting to see how teams of agents that were not trained together perform
  - If assembled teams perform well, we believe that would be strong evidence of collaboration



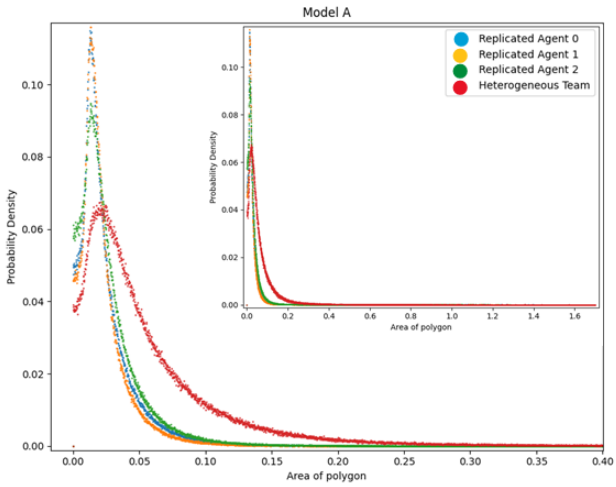
REFERENCES

[1] A. Tampuu, T. Matiisen, D. Kodelja, I. Kuzovkin, K. Korjus, J. Aru, et al. "Multiagent cooperation and competition with deep reinforcement learning," *PLoS ONE*, vol. 12, no. 4, 2017.
[2] R. Fernandez, E. Zaroukian, J. D. Humann, B. Perelman, M. R. Dorothy, S. S. Rodriguez, and D. E. Asher, "Emergent heterogeneous strategies from homogenous capabilities in multi-agent systems," Internal work-in-progress 2020.
[3] A. Nistala and J. Guttag, "Using deep learning to understand patterns of player movement in the NBA," *Proceedings of the MIT Sloan Sports Analytics Conference*, 2019.
[4] A. Santago, B. Colder, and K. Gemp, "Leveraging advances in spatial-temporal analytics for use in mission performance analysis," MITRE Corporation, Tech. Report. 18-4197, Dec. 2018.
[5] E. Zaroukian, S. S. Rodriguez, S. L. Barton, J. Schaffer, B. Perelman, N. R. Waytowich, et al. "Algorithmically identifying strategies in multi-agent game-theoretic environments", In SPIE Defense + Commercial Sensing, 2019.
[6] R. Lowe, Y. I. Wu, A. Tamar, J. Harb, O. P. Abbeel, and I. Mordatch, "Multi-agent actor-critic for mixed cooperative-competitive environments," in *Advances in neural information processing systems*, 2017, pp. 6379-6390.

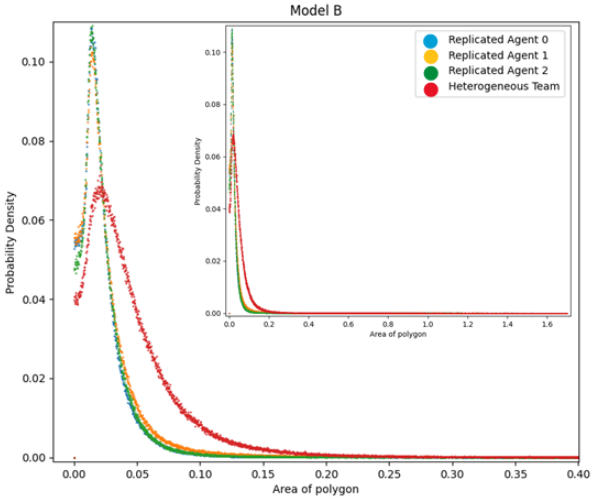
KMEANS CLUSTERING



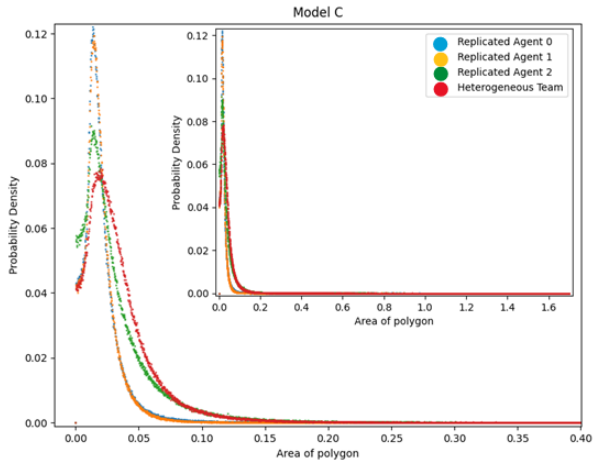
PREDATOR POLYGON AREA



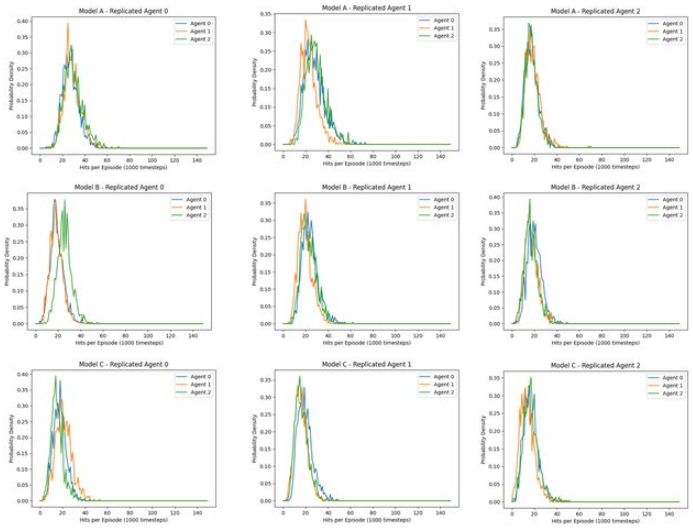
PREDATOR POLYGON AREA



PREDATOR POLYGON AREA



RESULTS



UNCLASSIFIED



APPROVED FOR PUBLIC RELEASE







U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Fluctuations in Social Experiences Shape Individual Decision-Making Under Risk

Eri Phinisee

Summer Student Researcher

CCDC-ARL HRED

06 Aug 2020

APPROVED FOR PUBLIC RELEASE

UNCLASSIFIED





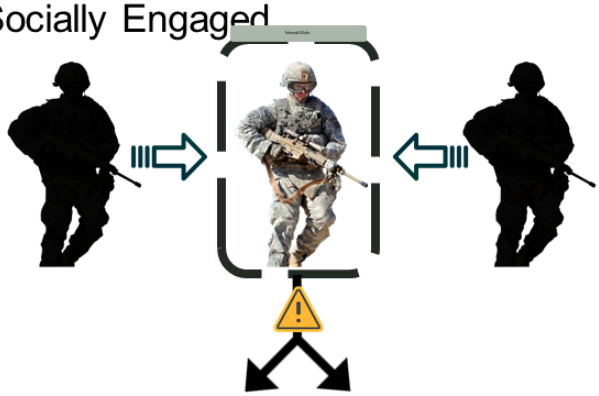
Personal Introduction





UNCLASSIFIED

Soldiers: Susceptible to Risk & Socially Engaged



UNCLASSIFIED

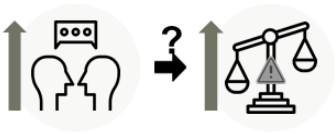
Introduction | Methodology | Analysis | Discussion

Social resources create a sense of strength against risk

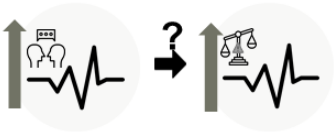


Research Questions

1. What are the effects of daily social interactions on risk-taking behavior?

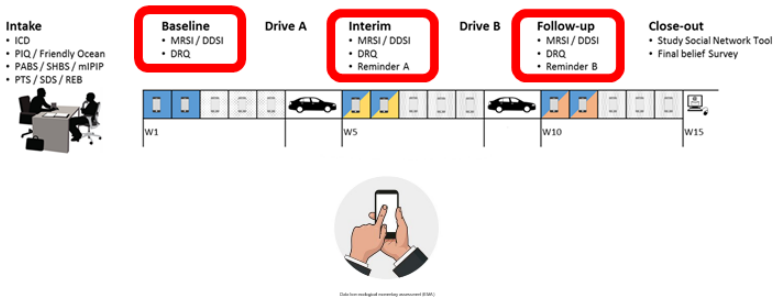


2. How does intraindividual variability in social interactions relate to intraindividual variability in risk-taking behavior?



UNCLASSIFIED

Real-World Driving Study



Introduction | Methodology | Analysis | Discussion

Risk-Taking

"You have recently been **successful** / **done poorly** in an online game. Now, you currently have a **SURPLUS**/**DEFICIT** of **+/-**$10 in your Game wallet. Choose the gamble that you want."



Introduction | Methodology | Analysis | Discussion

Social Interaction





Intraindividual Variability



Introduction | Methodology | Analysis | Discussion

Q1:

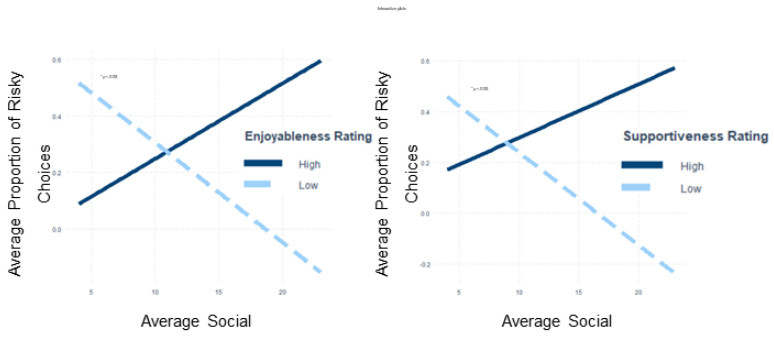


Social frequency & its interaction with enjoyableness/supportiveness are significant predictors of risk-taking in the gain domain.

UNCLASSIFIED

Introduction | Methodology | Analysis | Discussion

Q1:

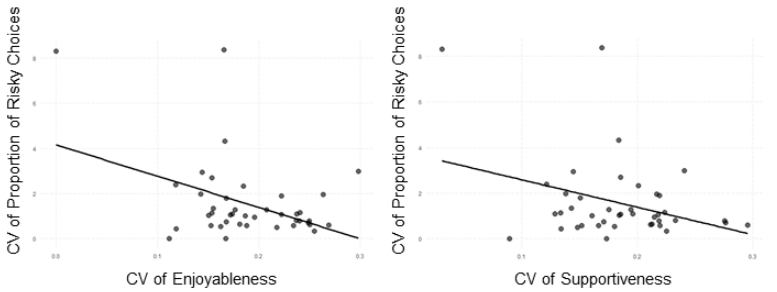


When social interactions are deemed unenjoyable/unsupportive, having more of them decreases risk-taking.

UNCLASSIFIED

Introduction | Methodology | Analysis | Discussion

Q2:



Subjects who experience varying levels of enjoyable/supportive social interaction engage in more consistent risk-taking behavior.

UNCLASSIFIED

31

UNCLASSIFIED

Introduction | Methodology | Analysis | Discussion

Q1

Q2

UNCLASSIFIED

32

Future Implications

- Given an environment where interactions between soldiers are likely to be brief and stressful, certain policies can be enacted to decrease/decrease the frequency of interactions in order to make soldiers more/less risk taking, depending on the demands of the mission.
- Soldiers familiar with each other should be grouped together to reduce mobility fluctuating risk taking behavior.



UNCLASSIFIED

Introduction | Methodology | Analysis | Discussion

Future Studies



Type of social interaction



Temporal effect



Loss aversion



Size of social network

Acknowledgements



ARL-HRED
Annenberg School for Communication, University of Pennsylvania



Journeyman Fellow at ARL
Doctoral candidate at School of Computing and Information, University of Pittsburgh

UNCLASSIFIED



U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND –
ARMY RESEARCH LABORATORY

Atomistic Probing of Catalytic Activities in H and O-Terminated Diamond (100) Surfaces

Jenille Cruz, Undergraduate
California State University, Fullerton
Dr. Mahesh Neupane, Mentor
RF and ICs Design Branch, Advanced Electronics Division

27 JUL 2020

UNCLASSIFIED//FOR OFFICIAL USE ONLY//DRAFT//PRE-DECISIONAL

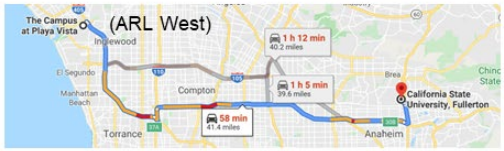
Outline

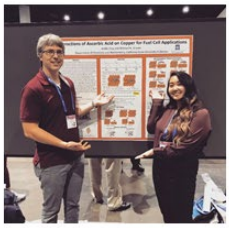
- Introduction
  - Hydrogen-Terminated Diamond (100)
- Motivation
  - Oxygen-related sites
- Objectives
  - Targets and goals
- Methods
  - How the data was obtained
- Results
  - Findings of this research
    - Energetically stable structures
    - Electronic properties
- Summary
  - Conclusion and future work

- **California State University, Fullerton**





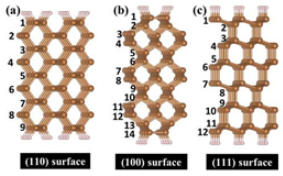


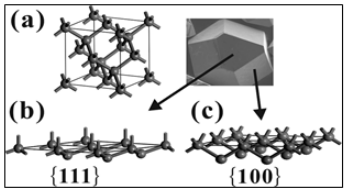


- **Undergraduate Senior**
- **Bachelor of Science in Chemistry**

Introduction

- **Diamond has distinctive features that make it superior from other semiconductors (GaN, Si, SiC):**
  Large band gap
  Higher electron/hole mobility
  Higher thermal conductivity
- **Commonly used for radio frequency (RF) applications and high powered control electronics suitable for Radar applications**
- **Diamond exhibits unique geometrical and electronic properties**

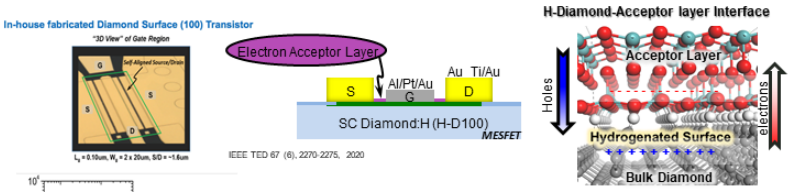


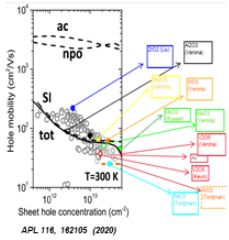


[1]Weil et al. JDR&E, 2019

Motivations

- Diamond is an insulator, so <u>doping them is challenging</u>.
- <u>Hydrogen-termination</u> is needed to induce <u>p-type doping</u> in insulating diamond surfaces for FET devices





Key Limiting Factors for Hole Mobility and Density:

1. <u>Quantity/Rate</u> of Electrons Transfer from H-Diamond to Acceptor Layer
2. Electron-Hole <u>Distance</u> (Coulomb Scattering)

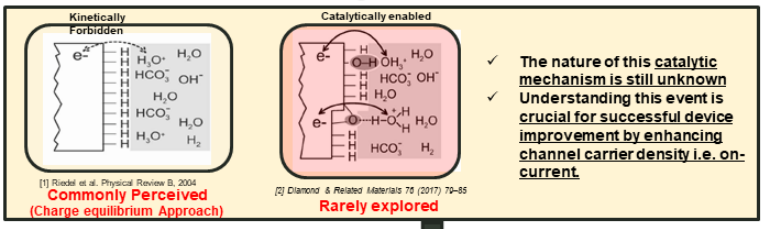
A trade-off exist between mobility and channel charge density at the surface

Higher Charge → Low Mobility (Due to carrier-carrier scattering)

UNCLASSIFIED

Motivations

2 Possible Charge Transfer Mechanisms

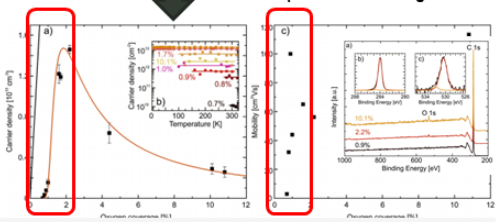


- ✓ The nature of this <u>catalytic mechanism is still unknown</u>
- ✓ Understanding this event is <u>crucial for successful device improvement by enhancing channel carrier density i.e. on-current</u>

[1] Qing et al. Diamond and Related Materials, 2019

Recent Experimental Findings

- ✓ Highest reported <u>carrier density and mobility</u> values for the hydrogenated diamond surface
- ✓ <u>Oxygen-related sites</u> are <u>catalytically</u> involved in the <u>transfer-doping mechanism</u>
- ✓ Charge density and mobility <u>increases</u> between 1-2% O2 on H-terminated Diamond Surface



<u>Potential Army's impact</u>: Efficient, high-frequency RF Transistor for Target Detection Applications

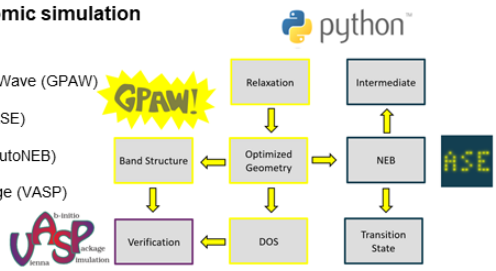
OBJECTIVES

- To study the effect of adsorbed H and O atoms on structural and electronic properties of H-terminated diamond (100) surface

- To determine the most favorable loading site of H and O atoms and calculate the most stable energy

Methodology

- **Quantum mechanical atomic simulation**
- *Density Functional Theory*
- Grid-Based Projector Augmented Wave (GPAW)
- Atomic Simulation Environment (ASE)
- Automated Nudge Elastic Band (autoNEB)
- Vienna ab initio Simulation Package (VASP)



Hamiltonian

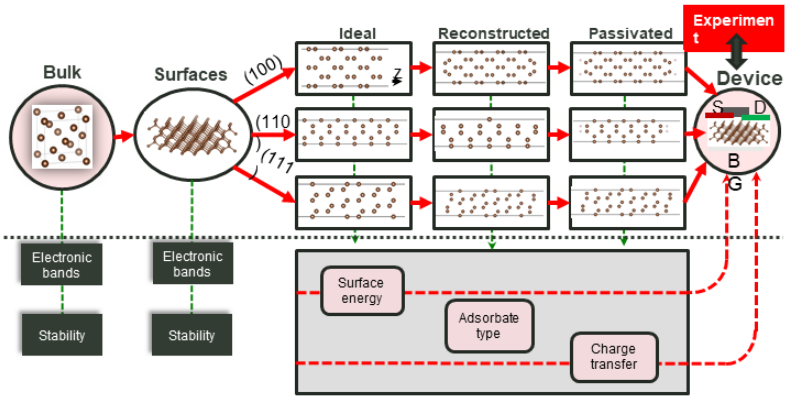
$$-\frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|}\,d\vec{r}' + \hat{V}_{xc} + \hat{V}_{ext}$$

$$\hat{H}_{KS} = \hat{T}_0 + \hat{V}_H + \hat{V}_{xc} + \hat{V}_{ext}$$

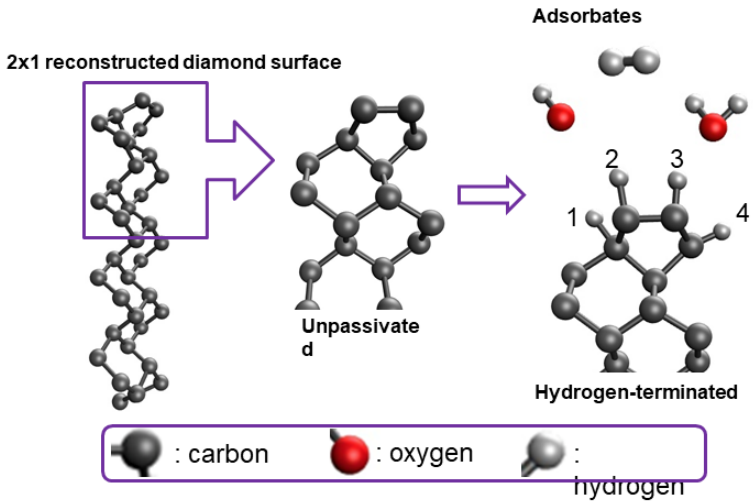
$$H[\rho] \equiv E_{V_{ext}}[\rho]$$

$$V_{xc}^{GGA}[\rho] = \int \rho(\vec{r})\,\epsilon_{xc}(\rho(\vec{r}), |\nabla\rho(\vec{r})|)\,d\vec{r}$$

Model design- Process FLow



Diamond (100) surface







Questions we would like to ASK..

- **What are the type of adsorbates that stick to the diamond (100) surface**
- **How do these molecules adsorb**
- **What is the energy of the adsorbed system**
- **What is the role of the adsorbate molecules in the atmosphere and their influence in the catalytic event in absence of hydrogen-termination**

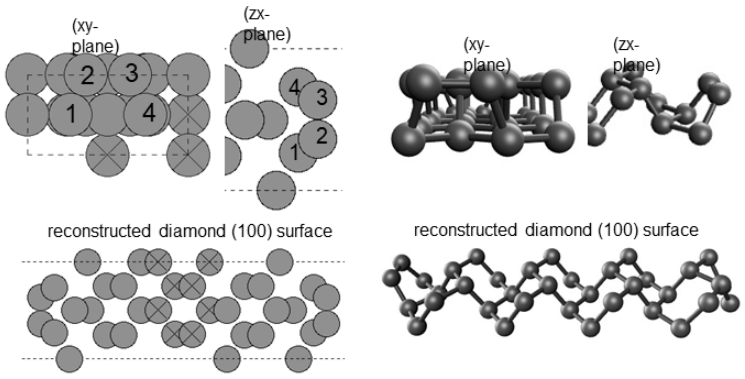
UNCLASSIFIED



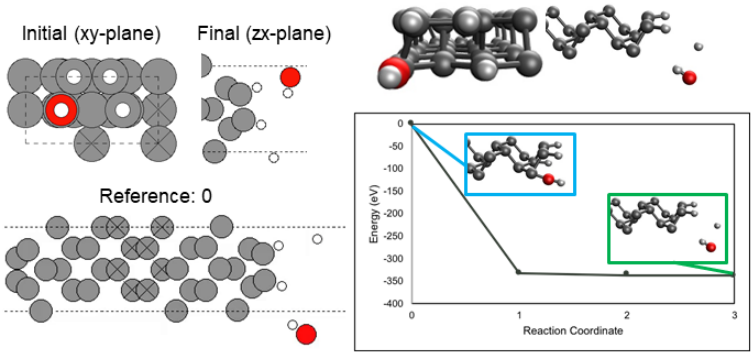


CASE 1: OH on H-Terminated Diamond (100)

Objective: To understand the role OH molecules in the hydrogenation process

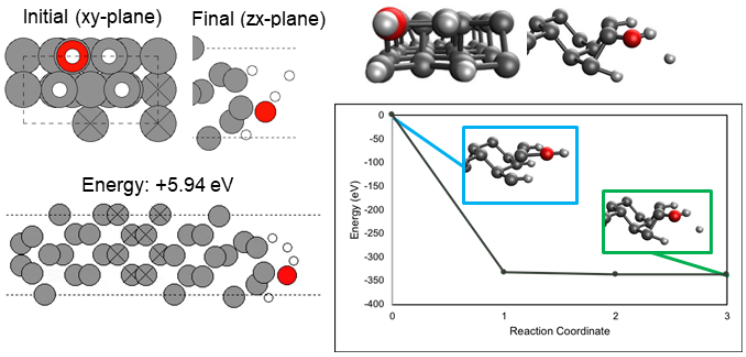


site 1



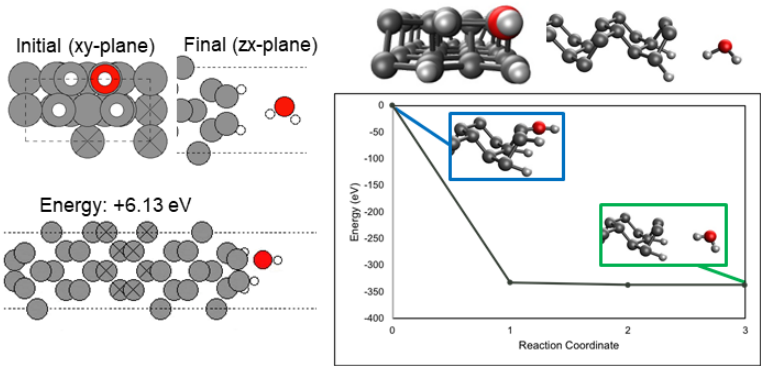
The OH group on site 1 and the H on site 4 repel from the surface

site 2



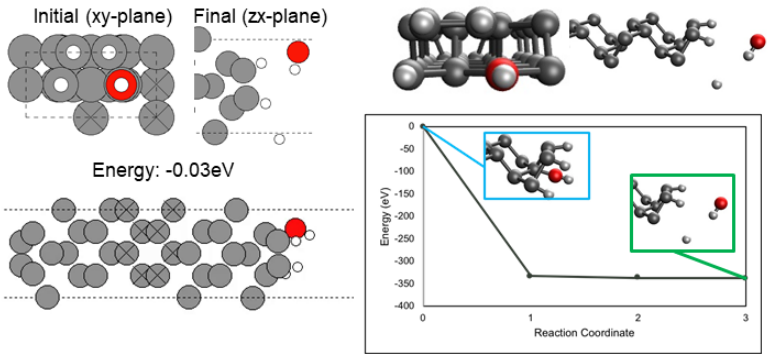
The OH group stays on site 2 and the H on site 4 repels away from the surface

site 3



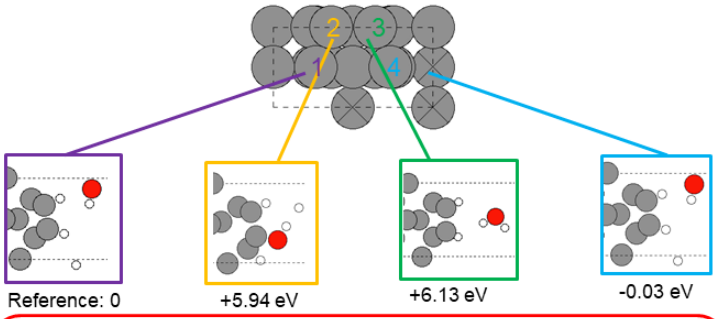
Hydrogens stay on site 1 and site 2 while H_2O molecule forms

site 4



The OH group on site 4 and the H on site 1 repels from the surface

recap

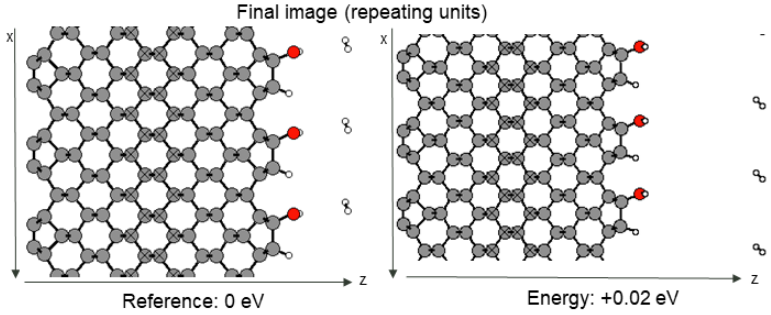


- Site 4 has the highest energy out of the 4 sites
- These 4 carbon atoms are sp^3 hybridized
- Due to steric hindrance, we find that certain atoms prefer to stay on the surface and some to repel
- Sites 1 and 4 are completely saturated, therefore sites 2 and 3 are easier to adsorb

CASE 2: H_2 ON H-TERMINATED DIAMOND (100)

Objective: To understand the role of H_2 in the hydrogenation process

Final image (repeating units)

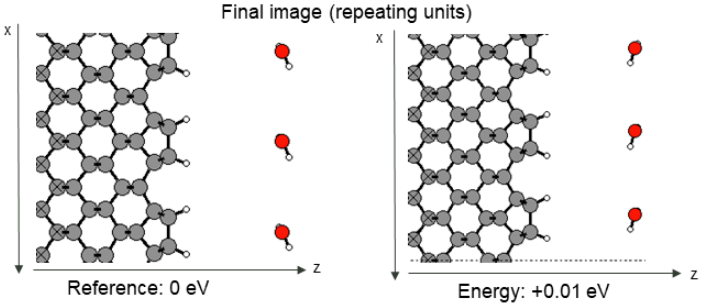


- We are studying the surface energy, adsorbate type, and charge transfer
- To understand how H_2 interacts with the surface and whether it leads to charge transfer mechanism

CASE 3: H_2O ON H-TERMINATED DIAMOND (100)

Objective: To understand the role of H_2O molecules in the hydrogenation process

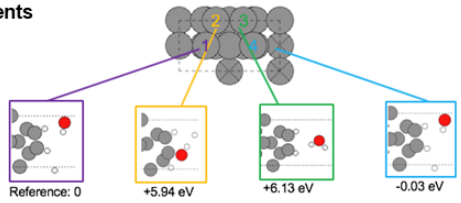
Final image (repeating units)



- In the atmosphere, there is an abundant of water molecules, so in this study we want to know how H_2O interacts with this hydrogenated surface
- Is there any catalytic involvement? Where do they adsorb?

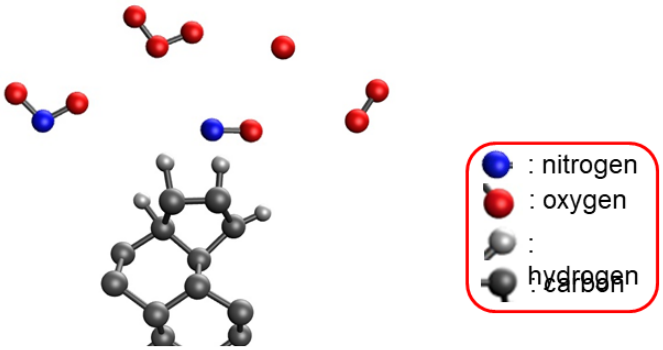
summary

- Provided insight of how OH, H_2 and H_2O molecules adsorbed the Diamond (100) surface
- Found the most favorable adsorption sites and calculated the most stable energies of these types of systems
- Site 2 and 3 were the preferred loading sites for all the molecules
- Based on our observations, we are in the process of analyzing this further
- Oxygen-related species could play a significant role in the catalytic mechanism, which warrants further investigation for successful device improvements



Future Plans

- To analyze other adsorbates on diamond (100) surfaces such as O, O_2, O_3, NO, and NO_2



Acknowledgements

- **DOD HBCU/MI Summer Program for financial support**
- **Mentors**

Dr. Mahesh Neupane (ARL West)

Dr. Michael Groves (CSUF)





U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Fuel Property Effects on Ignition

Alyssa Hawe

Summer Intern

University of Illinois at Urbana Champaign

08 06 2020

DISTRIBUTION STATEMENT GOES HERE

UNCLASSIFIED

Presentation Outline

- **Introduction**
  What is Fuel?
  Real vs. Surrogate Fuels
  Ignition delay and fuel conditions
  Types of mechanisms
- **Objectives**
  Goals and methods
- **Results**
  Single species fuel: n-Heptane
  Real Jet A fuel surrogates
  Lumped Mechanism: C11H22
- **Conclusion**
  Summary of work
  Future Considerations





INTRODUCTION

- What is Fuel?
- Real vs. Surrogate Fuels
- Fuel Conditions and Ignition Delay
- Types of Mechanisms

What is fuel?

Fuel: any material that can be burned to produce heat or power

- Fuels are composed of mixtures of hydrocarbons
- Main fuel property is its autoignition quality



Why is Researching Fuel Important?

- Fuel research for the U.S. Army is important for the development of new ignition systems and engines
- Understanding the impact of chemistry on different fuels is important for future Army systems to operate from a range of local source fuels

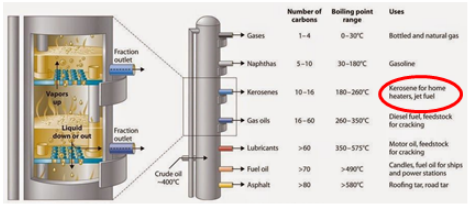
Single-Fuel Concept:
A single fuel is used for all equipment to simplify fuel operations. The U.S. Army currently uses JP-8 jet fuel.

JP-8 Uses



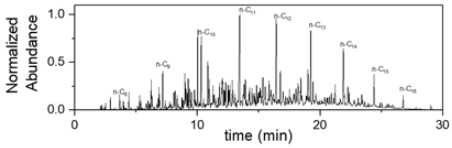


Fuel distillation



- Military uses Kerosene fuels
  - Jet fuels vary depending on chemical composition
    - Hundreds of different components

Real Fuel Composition: Jet A GC/MS result



- **GC/MS:** Gas chromatography–mass spectrometry
- Each peak indicates each individual species in the fuel

Real vs. Surrogate Fuel

Real Fuel vs. Surrogate Fuel:

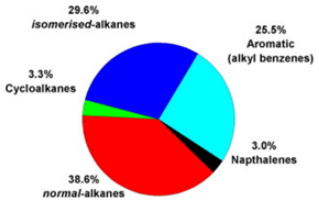
- **Real Fuel**
  - Jet aviation, diesel, and gasoline fuels are considered real fuels
  - Complex mixtures of hundreds of chemical compounds
    - Too many fuel components to model
  - To get around this issue, surrogate fuels are modeled instead

- **Surrogate Fuel**
  - A mixture of a select number of components that are still capable of reproducing similar physical and chemical properties of interest in its real fuel counterpart

Why are surrogates used?

- Reduces computation time to model
- Fewer chemical species

Jet-A POSF 4658 Real Fuel Composition



Reference: https://doi.org/10.1016/j.combustflame.2011.11.002

Jet A Surrogate Generation 2

Fuel	Chemical Formula	Mole Fraction (%)
n-dodecane	NC12H26	40.41
iso-octane	IC8H18	29.48
n-propylbenzene	PHC3H7	22.83
1,3,5-trimethylbenzene	C9H12	7.28

Fuel Conditions AND IGNITION DELAY

Fuel + Oxidizer (Air) → $CO_2 + H_2O (+ N_2)$

Equivalence Ratio (Φ, Phi):
Fuel to oxidizer ratio

Φ > 1 : More fuel than air (Rich condition)

Φ = 1 : Equal parts of fuel to air (Stoichiometric condition)

Φ < 1 : Less fuel than air (Lean condition)

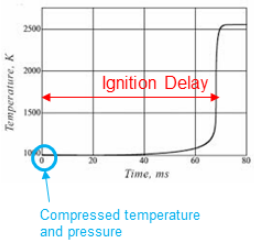
Compressed Pressure:
Initial pressure of the system after the air/fuel mixture is compressed

Compressed Temperature:
Initial temperature of the system after the air/fuel mixture is compressed

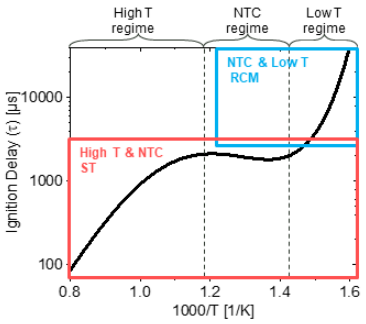
Ignition Delay (tau):
Interval of time between the start of injection of the fuel until ignition occurs.

3 Ways to Calculate Ignition Delay:

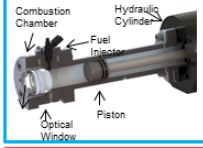
1) **Time vs. Pressure Graph**
   1) Ignition time based on inflection point or elevation of pressure to a designated point
2) **Time vs. Temperature Graph**
   1) Ignition time based on infection point
3) **Time vs. OH Concentration Graph**
   1) Ignition time based on maximum peak of OH



Experimental investigation of ignition delay

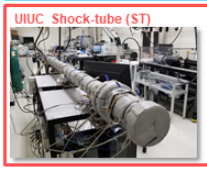


UIUC RCM (Rapid Compression Machine)



- T_c=600 to 850 K
- P_c=1 to 50 bar
- τ: 3 – 100 ms
- Fuel Charging: Fuel is directly evaporated inside the test chamber using direct test chamber (DTC) method
- Compression: Pneumatically driven, hydraulically stopped

UIUC Shock-tube (ST)



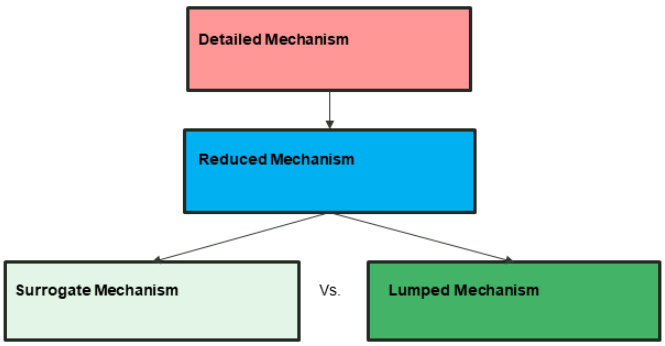
- T_c=750 to 1500 K
- P_c=1 to 70 bar
- τ: 0.1 – 8 ms
- Fuel Charging: External Fuel Mixing Vessel with magnetic Stirrer (heated)
- Compression: an incoming and reflected normal shock wave, caused by a driver gas

- High temperature oxidation:
  Chemistry is very fast, fuel decomposition
- NTC(Negative Temperature Coefficients):
  a decrease in reaction activity with an increase in temperature.
- Low temperature oxidation:
  Prediction of low temperature chemistry requires a perfect understanding of reaction pathways (mechanism), and fuel chemistry: not feasible

TYPES OF Mechanisms

Chemical Kinetic Mechanism:

Has species with related thermodynamic and transport characteristics and elementary chemical reactions with associated rate constants that explains how a chemical reaction occurs.



UNCLASSIFIED

OBJECTIVES

Goals and Methods

goals and Methods

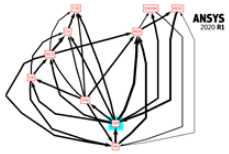
Objective: Use CHEMKIN to analyze fuel autoignition for the purpose of compression ignition

Research Goal: Assist in building up a database of kinetic models with a wide range of ignition properties being used in the **VICTOR Essential Research Program**

- **Versatile taCTical pOwer and pRopulsion (VICTOR) Essential Research Program (ERP)**
  - Multi-fuel Capable Hybrid Electric (MCHEP)
- **Program Goal:** Achieve multi-fuel capable compression ignition engines at altitude ambient conditions

CUP
CENTER FOR UAS PROPULSION
cup.illinois.edu

Research Tasks:
- Use CHEMKIN to conduct ignition delay simulations of various chemical kinetic models provided by UIUC
- Conduct species flux analysis and sensitivity analysis of select operation points
- Conduct analysis of data with focus on reaction pathways at low temperatures



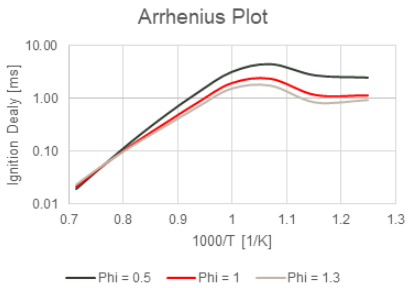
How my research and work will help:
- Understanding different fuel property effects on ignition will help further the development of new ignition systems and engines for the Army

UNCLASSIFIED

RESULTS

Single Species Fuel: n-Heptane

N-HEPTANE: Reduced mechanism



↑ Equivalence Ratio,
↓ Ignition Delay

Compressed Pressure: 20 bar

Compressed Temperature: 1400-800K

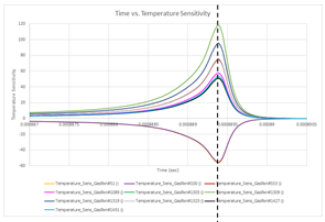
Fuel Mixture	Oxidizer Mixture	Complete-Combustion Products
NC7H16 (1.0)	N2 (0.79)	CO2
	O2 (0.21)	H2O
		N2

Fuel + Oxidizer (Air) → $CO_2 + H_2O$ (+ N_2)

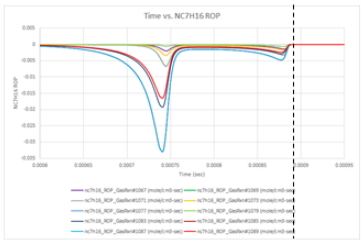
Temperature Sensitivity & ROP

Temperature Sensitivity:

- **Positive Sensitivity Coefficient**
  - Increasing rate of the reaction will lead to a **higher temperature** (more heat production
- **Negative Sensitivity Coefficient**
  - Increasing the rate of the reaction will lead to a **lower temperature** (less heat production or heat absorption)



Rate of Production (ROP):
The rate at which a product is produced by a reaction over a period of time.



800K, Ignition Delay = 0.8894 ms

RESULTS

Jet A Surrogate Fuels vs. C11H22 Lumped Mechanism

Jet A surrogate fuels

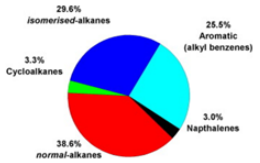
Jet A Surrogate Generation 1

Fuel	Chemical Formula	Mole Fraction (%)
n-decane	NC10H22	42.7
iso-octane	IC8H18	33.0
toluene	C6H5CH3	24.3

Jet A Surrogate Generation 2

Fuel	Chemical Formula	Mole Fraction (%)
n-dodecane	NC12H26	40.41
iso-octane	IC8H18	29.48
n-propylbenzene	PHC3H7	22.83
1,3,5-trimethylbenzene	C9H12	7.28

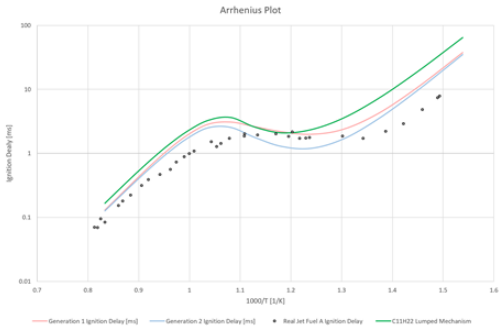
Jet-A POSF 4658 Real Fuel Composition



Reference: https://doi.org/10.1016/j.combustflame.2011.11.002

Conditions	Value
Equivalence Ratio (Phi)	1.0
Pressure	20 atm
Temperature	1200-650K

Surrogate & Lumped Mechanisms



* Points on graph are real jet fuel A experimental ignition delay values

Computation Time:

1. Gen 2 Surrogate
   1. ~3 hours
2. Gen 1 Surrogate
   1. ~ 2.5 hours
3. Lumped Mechanism (C11H22)
   1. ~5 min

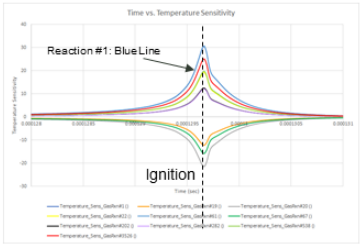
*** C11H22 was modeled using a lumped mechanism**

*** Generations 1 & 2 surrogate fuels were modeled using a surrogate mechanism**

High Temperature Combustion

Gen 1 Surrogate

1200K, Ignition Delay: 0.1297 ms

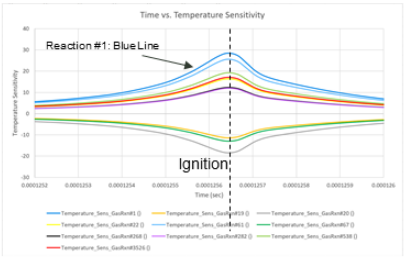


Very Important Reaction for High Temperature Combustion:

- **Reaction #1:** $H + O_2 \rightarrow O + OH$
  - Positive TSC

Gen 2 Surrogate

1200K, Ignition Delay: 0.1257 ms



Other Important Reactions:

- **Reaction #61:** $CH_3 + HO_2 \rightarrow CH_3O + OH$
  - Positive TSC
- **Reaction #67:** $CH_3 + HO_2 \rightarrow CH_4 + O_2$
  - Negative TSC

CONCLUSIONS

Summary of Work & Future Considerations

Summary of work

Conclusions:

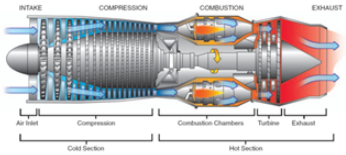
- Different combustion conditions affect the ignition process
- It is important to do sensitivity and ROP analysis at high and low temperatures
  - In **high temperature** combustion there is a rapid increase in temperature at ignition
  - In **low temperature** combustion there is a more gradual increase in temperature before the large spike in temperature at ignition
- At **high temperatures**, oxygen participates in the reaction after some decomposition is processed
  - H abstraction is much more like fuel decomposition
    - Example in n-Heptane combustion: $C_7H_{16} \rightarrow C_4H_8 + C_3H_7 + H$
- At **low temperatures**, the fuel reacts with oxygen first
  - H atom is abstracted from fuel molecule
    - Example in n-Heptane combustion: $C_7H_{16} \rightarrow C_7H_{15} + H$

Important Reactions:

- **High Temp Combustion:**
  - $H + O_2 \rightarrow O + OH$
- **Low Temp Combustion:**
  - $H + O_2 \rightarrow HO_2$
  - $2HO_2 \rightarrow H_2O_2 + O_2$

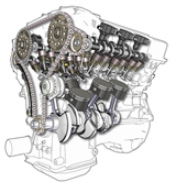
Future Considerations & Applications

Applications of Combustion Kinetics of Jet Fuels



Gas-turbine and automotive engines:

- CFD-based design
  - CFD = Computational fluid dynamics
- Pollutant emission
- Ignition



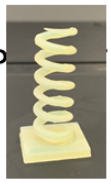
Future Considerations:

- Analyze cutting edge mechanism, HyChem, and recently developing mechanism from UIUC



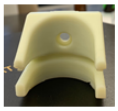
APPROVED FOR PUBLIC RELEASE

U.S. ARMY COMBAT CAPABILITIES DEVELOP
COMMAND –
ARMY RESEARCH LABORATORY





**Development of a Toughened Thermoset Vinyl Ester Photolithography Re
Performance Additive Manufacturing (AM)**



Jaclyn McLaughlin

Co-Op Polymer Scientist for Development of Polymer AM Materials

WMRD-MMRD

Distribution A. Approved for Public Release

06 AUGUST 2020

APPROVED FOR PUBLIC RELEASE

UNCLASSIFIED

Army Need for Renewable Resins and Polymer AM

- **Manufacturing at the Point of Need:** Can give the soldier the ability to make and use material as needed.
- **Army unique applications:**
  - Sustainability, mobility, lethality, and survivability applications.
  - Improve the properties and quality of additively manufactured high-performance polymers and composites to enable these unique applications.

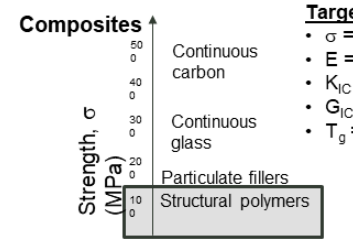




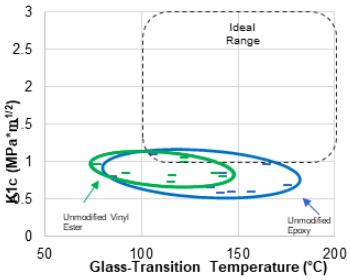
Mission: Develop advanced polymeric materials, lean manufacturing technologies, and intelligent design tools for producing Army material on-demand and by-design at the tactical point of need for structural, energetic, and responsive materials needs.

UNCLASSIFIED

Property and Manufacturing Targets

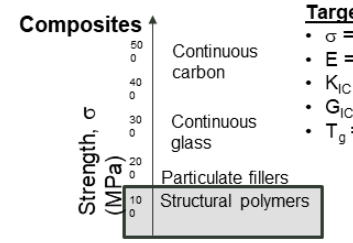


Target:
- σ = 110-500 MPa
- E = 2.5-100 GPa
- K_{IC} ≥ 1 MPa*$m^{1/2}$
- G_{IC} = 500-6000 J/m^2
- T_g = 110-300°C

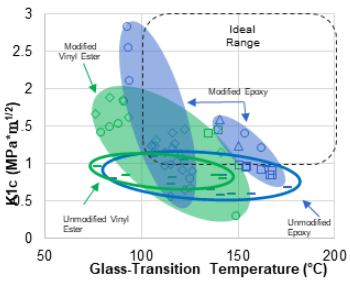




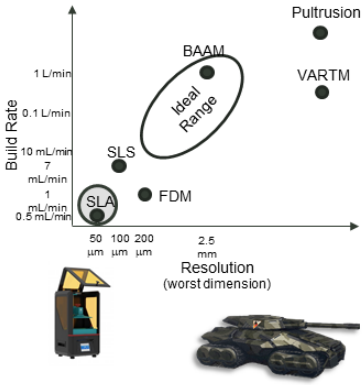
Property and Manufacturing Targets



Target:
- σ = 110-500 MPa
- E = 2.5-100 GPa
- K_{IC} ≥ 1 MPa*$m^{1/2}$
- G_{IC} = 500-6000 J/m^2
- T_g = 110-300°C



Target:
- 10-1000 mL/min
- 0.2-3 mm resolution



UNCLASSIFIED

Project motivations

•**It is well-known that second phase toughening via liquid rubber modification can greatly enhance thermoset toughness.** 1-8, 10-11

- **However, this has yet to be applied to the brittle, high-performance vinyl ester (VE) thermosets produced by AM.**
  - Rapid cure schedules of most photo-sensitive resins
  - Limitations on overall bulk viscosity based on processing method
  - Low resin compatibility with common modifiers

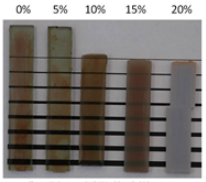
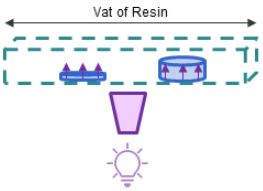


Figure 19: Post cured VE 828 with varied BR content.





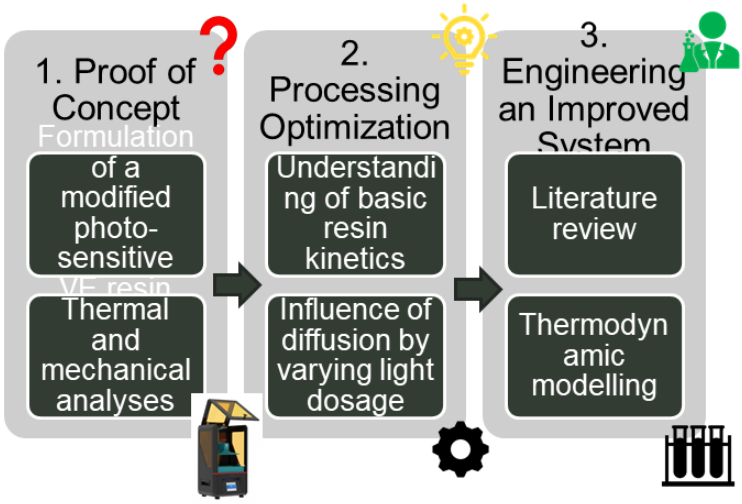
Goal: develop a toughened photolithography resin using a second phase toughener to improve the toughness of additively manufactured thermosets for high-performance applications.

UNCLASSIFIED

89

UNCLASSIFIED

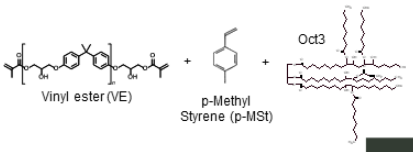
Project motivations and approach

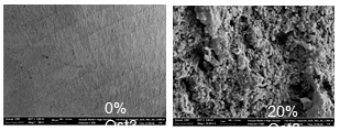


UNCLASSIFIED

90

1. Proof of concept





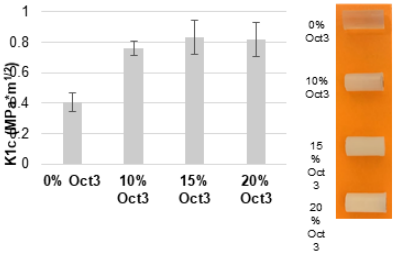
Formulation	E" T_g (°C) Thermally Cured[8]	E" T_g (°C) UV Cured	Flexural Modulus (GPa)
0% Oct3	138	145	3.1 ± 0.12
10% Oct3	115	109	2.7 ± 0.03
15% Oct3	112	105	2.7
20% Oct3	106	101	2.6 ± 0.06

•Toughening AM resins can be achieved using a second-phase toughener that relies on phase separation.

Phase separation observed by opacity of printed samples and SEM.

Toughness (K_{1c}) of all modified samples is improved from the neat resin.

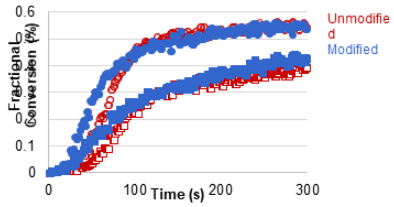
Some decline in thermal and mechanical properties (plasticization, lower crosslink density, and Rule of Mixtures).

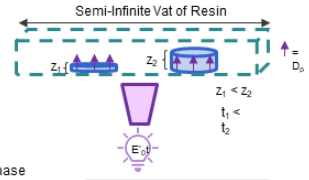


A. Grous. (2011). Toughening Bimodal Vinyl Ester Blends Using Bio Rubber Monomers. Philadelphia: Drexel University Department of Chemical Engineering.

2. Processing optimization

- **Basic resin kinetics not significantly affected by presence of Oct3.**
- **Phase separation is impacted by print layer thickness because of imposed dose rate gradients affecting the degree of kinetic trapping of Oct3.**
  - Differences in phase separation confirmed by SEM and dynamic mechanical analysis (DMA).
  - Effects of phase separation on toughness properties was not significantly obvious from these results.

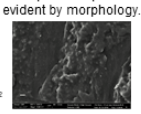




$$E_0' t * \exp(-z/D_p) = E_z$$

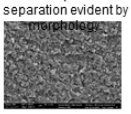
z = layer height
E_0 = energy density of incident light
E_z = applied energy density
D_p = photo-curing sensitivity of ink

Less phase separation evident by morphology.



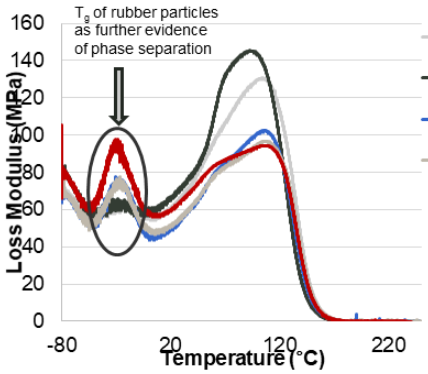
z_1 = 0.025 mm
t_1 = 8.49 s
E_{z1} = 23.3 mJ/cm²

More phase separation evident by morphology.



z_2 = 0.3 mm
t_2 = 22.8 s
E_{z2} = 8.70 mJ/cm²

Thermal performance of toughened Ve – influence of processing conditions

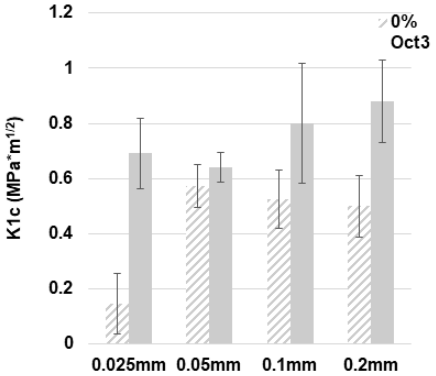


Significant plasticization of the modifier occurs.

Layer Thickness (mm)	T_g 0% (°C)	T_g 20% (°C)
0.025	135	102
0.05	140	104
0.1	140	106
0.2	--	107
0.3	--	107

- Rubbery E'' from particles increases as layer thickness is increased, indicating more phase separation has occurred.
- Primary phase T_g of modified samples unaffected.

mechanical performance of toughened Ve – influence of processing conditions

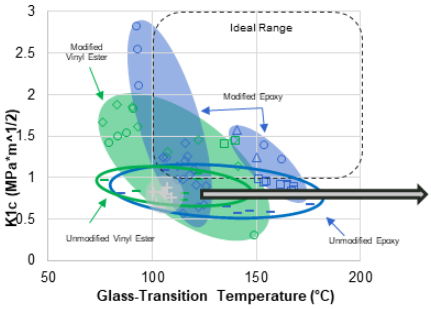


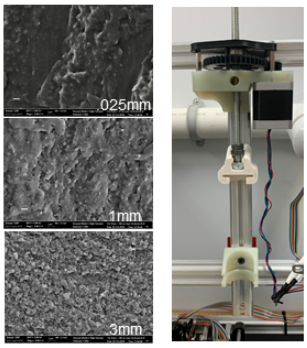
- The presence of the rubber modifier, at all layer sizes, increases the fracture toughness properties of the material.
- Effects of phase separation on toughness properties is not significantly obvious from these results.
- Plasticization likely results in the increase of fracture toughness at all layer sizes.

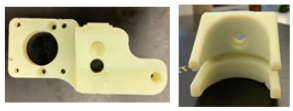
3. Engineering an improved system

- **We now know toughening AM resins can be achieved using a second-phase toughener that relies on phase separation.**
- **Engineer new system based on this data and a thermodynamic model to produce a resin exhibiting better phase separation behavior and enhanced toughness properties.**

Looking for earlier onset of phase separation and decrease in rubber plasticization.

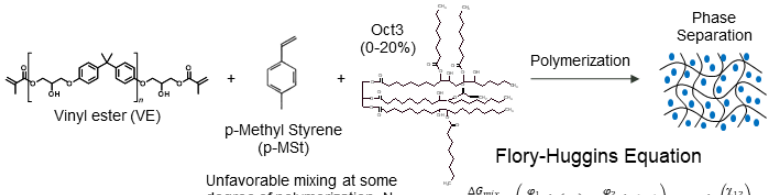






UNCLASSIFIED

Predicting Phase Separation – Thermodynamics



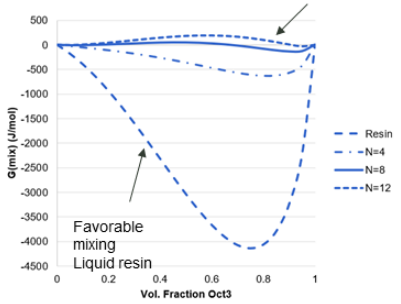
Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$

Interaction Parameter

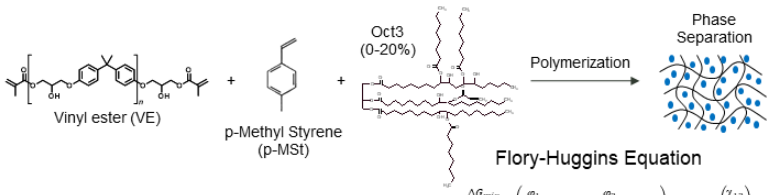
$$\chi_{12} = v_s(\delta_2 - \delta_1)^2/RT$$

Unfavorable mixing at some degree of polymerization, N



- **No phase separation at room temperature.**
- **As the degree of polymerization for the network increases (N), unfavorable mixing conditions arise, driving the phase separation of the modifier.**

Predicting Phase Separation – Thermodynamics

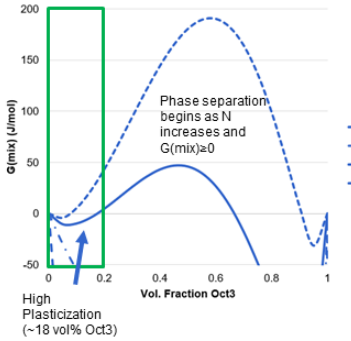


Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$

Interaction Parameter

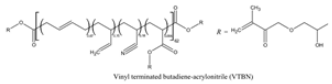
$$\chi_{12} = v_s(\delta_2 - \delta_1)^2/RT$$



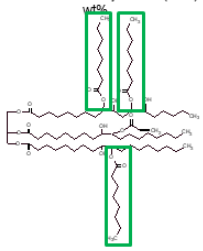
- **No phase separation at room temperature.**
- **As the degree of polymerization for the network increases (N), unfavorable mixing conditions arise, driving the phase separation of the modifier.**

Engineering the Bio-rubber to Maximize Phase Separation

- **Bio-based rubbers are being developed by several research groups in an effort to move away from petroleum-based toughners.** [1-8]
- **One way to improve the phase separation behavior observed in these systems, the alkyl chains on Oct3 can be changed.** [6,7]
- **How does this apply to the thermodynamic model?**



Petroleum-based modifiers based on terminated butadiene acrylonitrile (TBN) 0-12 wt%



Bio-based modifiers based on epoxidized soybean oil (ESO) or other triglycerides

Flory-Huggins Equation

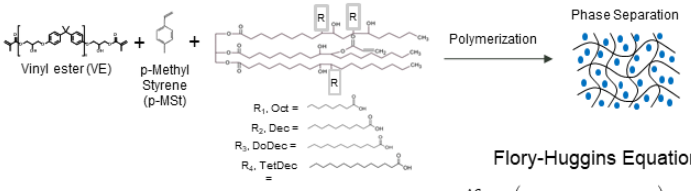
$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$

Interaction Parameter

$$\chi_{12} = \frac{v_s(\delta_2 - \delta_1)^2}{RT}$$

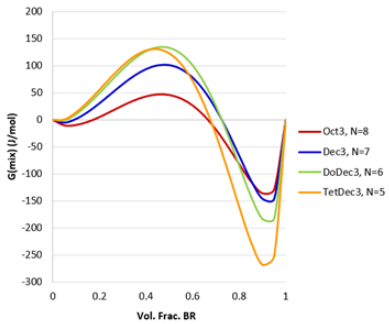
E. J. Robinette et al., *Polymer*, 45 (2004) 6143-6154.
J.S. Ullett et al., *Polymer Engineering & Science*, 35:13 (1995) 1086-1097.
E. Dreezen et al., *Journal of Applied Polymer Science*, 72:5 (1999) 647-657.
H. Kargarzadeh, *Journal of Applied Polymer Science*, 132 (2015) 41292.
G. Bachet et al., *Polymer Journal*, 52 (2020) 345-357.
S. Yadav et al., *ACS Omega*, 3 (2018) 2641-2653.
N. Gong. (2010). Philadelphia: Drexel University. Department of Chemical Engineering.
A. Gross. (2011). Philadelphia: Drexel University. Department of Chemical Engineering.

Engineering the Bio-rubber to Maximize Phase Separation



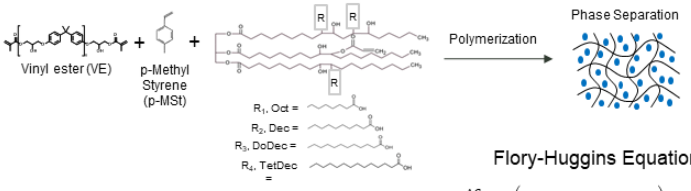
Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$



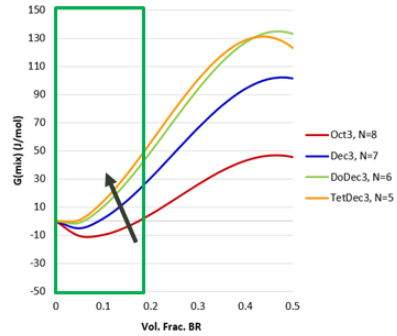
- **Changing the length of the fatty acid alkyl chains do not significantly affect bio-based rubber solubility within region of interest.**
- **Earlier onset of phase separation is observed when length of fatty acid alkyl chain is increased.**

Engineering the Bio-rubber to Maximize Phase Separation



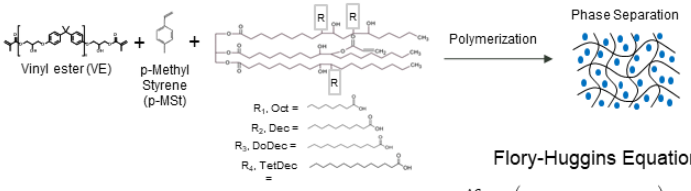
Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$



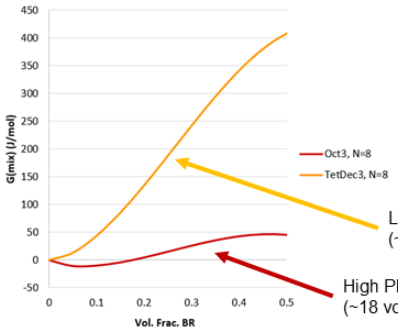
- **Longer fatty acid chains reduce the value of N required for the onset of phase separation.**
- **Earlier onset of phase separation is observed when length of fatty acid alkyl chain is increased.**

Engineering the Bio-rubber to Maximize Phase Separation



Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$



- **Longer fatty acid chains decrease the content of modifier that is plasticized within the network.**

Engineering the ve oligomer to Maximize Phase Separation

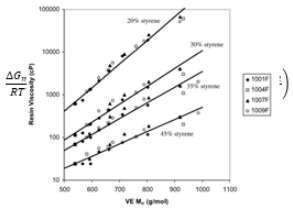
•By increasing the molecular weight (MW) of VE oligomers, the resultant network becomes more ductile. [9-11]
Increases material toughness

- **A ductile network is most effectively toughened by the presence of rubbery particles.** [10,11]
- **Something to look out for: increasing the MW of VE oligomers will also increase the viscosity of the resin.**
  - Bimodal blends of various VE oligomers can alleviate this effect. [9]
- **How does this apply to the thermodynamic model?**



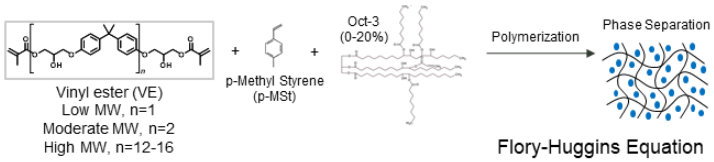
High crosslink density resulting in material brittleness

Low crosslink density resulting in material toughness



J.J. La Scala et al., *Polymer*, 46 (2005) 7908–7921.
A.F. Yee, and R.A. Pearson, *Journal of Materials Science*, 24 (1989) 2571–2580.
M.L. Auad et al., *Journal of Materials Science*, 37 (2002) 4117–4126.

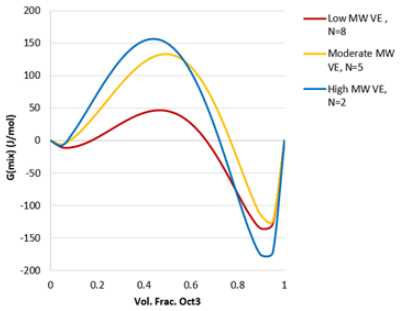
Engineering the ve oligomer to Maximize Phase Separation



Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$

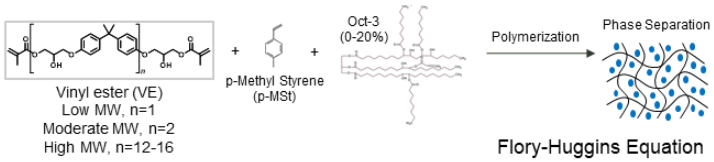
n = number of repeat units
N= degree of polymerization



- **Increasing the MW of VE oligomers do not significantly affect bio-based rubber solubility within region of interest.**
- **Earlier onset of phase separation is observed when MW of the VE is increased.**

UNCLASSIFIED

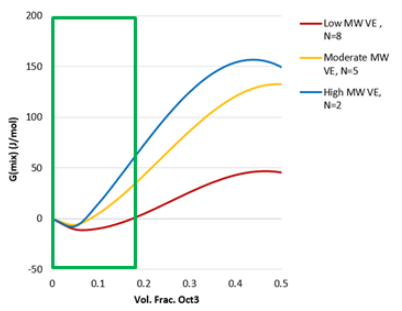
Engineering the ve oligomer to Maximize Phase Separation



Flory-Huggins Equation

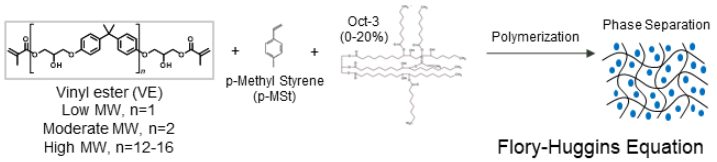
$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2 \ln\left(\frac{\chi_{12}}{v_s}\right)$$

n = number of repeat units
N= degree of polymerization



- **Higher MW VEs reduce the value of N required for the onset of phase separation.**
- **Earlier onset of phase separation is observed when MW of the VE is increased.**

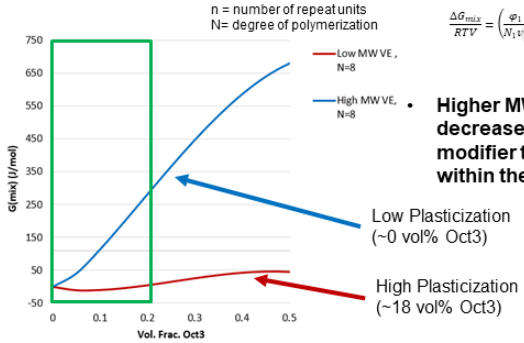
Engineering the ve oligomer to Maximize Phase Separation



Flory-Huggins Equation

$$\frac{\Delta G_{mix}}{RTV} = \left(\frac{\varphi_1}{N_1 v_1}\ln(\varphi_1) + \frac{\varphi_2}{N_2 v_2}\ln(\varphi_2)\right) + \varphi_1\varphi_2\ln\left(\frac{\chi_{12}}{v_s}\right)$$

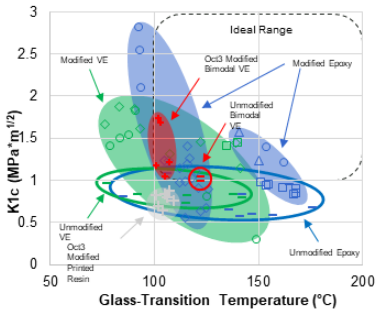
n = number of repeat units
N= degree of polymerization



- **Higher MW VE oligomers also decrease the content of modifier that is plasticized within the network.**

future work and COOP Experience

- **By altering the structure of the rubber modifier and VE crosslinker used in our resin formulation, the properties of high-performance VE produced by AM will likely be improved.**



Future Experiments

- SEM of fracture surface on all current samples and quantify observed mesoscopy.
- Test hypothesis of using the TetDec3 modifier and bimodal blends to achieve maintenance of T_g and improvements in fracture toughness (K_{1c}) properties.
  - Print samples
  - SEM imaging and analysis
  - Measure material properties (T_g and K_{1c})

future work and COOP Experience

What I've Gained From My Time at ARL…

- [ ] March 31, 2020 – September 18, 2020
- [ ] Data analysis of previously attained data.
- [ ] Improve upon presentation skills by providing weekly updates.
- [ ] Critical reading of academic literature.
- [ ] Opportunity to learn more about ongoing research by attending virtual meetings and seminars.
- [ ] Technical writing skills by participating in ARL-Drexel collaboration review article.

Thank You!

Questions? Comments?



References

[1] E.J. Robinette, E.J. Zaiee, and G.R. Palmese. "Toughening of vinyl ester resin using butadiene-acrylonitrile rubber modifiers", *Polymer*, 45 (2004) 6143-6154.
[2] J.S. Ullett, and R.P. Chartoff. "Toughening of unsaturated polyester and vinyl ester resins with liquid rubbers", *Polymer Engineering & Science*, 35:13 (1995) 1086-1097.
[3] E. Dreerman, M. Narkis, A. Siegmann, R. Joseph, H. Dodiuk, and A. Dibenedetto. "Mechanical behavior and structure of rubber modified vinyl ester resins", *Journal of Applied Polymer Science*, 72:5 (1999) 647-657.
[4] H. Kargarzadeh. "Functionalized Liquid Natural Rubber and Liquid Epoxidized Natural Rubber: A Promising Green Toughening Agent for Polyester", *Journal of Applied Polymer Science*, 132 (2015) 41292.
[5] Q. Bach, C.M. Vu, H.T. Vu, and T.V. Dieu. "Epoxidized soybean oil grafted with CTBN as novel toughener for improving the fracture toughness and mechanical properties of epoxy resin", *Polymer Journal*, 52 (2019) 345-357.
[6] S. Yadav, F. Hu, J.J. La Scala, and G.R. Palmese. "Toughening Anhydride-Cured Epoxy Using Fatty Alkyl-Anhydride-Grafted Epoxidized Soybean Oil", *ACS Omega*, 3 (2018) 2641-2651.
[7] X. Geng. (2010). Design of Epoxidized Soybean Oil Based Bio-rubber for Vinyl Ester and Unsaturated Polyester Resin Toughening. Philadelphia: Drexel University Department of Chemical Engineering
[8] A. Grous. (2011). Toughening Bimodal Vinyl Ester Blends Using Bio-Rubber Monomers. Philadelphia: Drexel University Department of Chemical Engineering.
[9] J.J. La Scala, J.A. Orlicki, C. Winston, E.J. Robinette, J.M. Sands, and G.R. Palmese. "The use of bimodal blends on vinyl ester monomers to improve resin processing and toughen polymer properties", *Polymer*, 46 (2005) 2908-2921.
[10] A.F. Yee, and R.A. Pearson. "Toughening mechanisms in elastomer-modified epoxies", *Journal of Materials Science*, 24 (1989) 2571-2580.
[11] M.L. Auad, J. Borrajo, and M.I. Aranguren. "Rubber modified vinyl ester resins of different molecular weights", *Journal of Materials Science*, 37 (2002) 4117-4126.

mechanical performance of toughened Ve – influence of processing conditions

	Neat System 0 wt% Oct-3		Modified System 20 wt% Oct-3	
Layer Thickness (mm)	Flex Modulus (GPa)	Max Flex Strength (MPa)	Flex Modulus (GPa)	Max Flex Strength (MPa)
0.025mm	3.49 ± 0.088	100 ± 17.4	2.73 ± .205	96.4 ± 8.63
0.05mm	3.04 ± 0.057	113 ± 13.7	2.52 ± .028	85.2 ± 7.81
0.1mm	3.18 ± 0.19	121 ± 24.8	2.50 ± 0.038	77.5 ± 9.40
0.2mm	2.3 ± 0.063	62.5 ± 24.3	2.45 ± 0.131	72.9 ± 13.5
0.3mm	1.91 ± 0.127	82.5 ± 7.04	2.03 ± 0.194	66.1 ± 15.6

For 0.2mm and 0.3mm samples, the flexural properties of both systems appear similar

For 0.025mm – 0.1mm, the neat system has higher flexural properties than the modified system

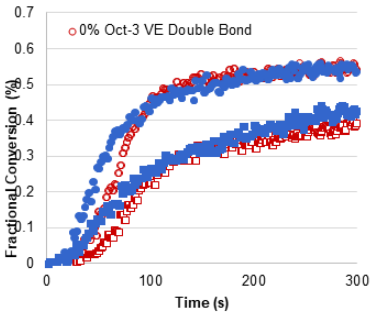
Increased phase separation results in lower flexural properties as layer thickness of the print is increased

It is known that the presence of soft, rubbery, particles within the matrix decrease the mechanical properties of these modified thermosets

- Decline in crosslink density
- Rule of Mixtures

How is does the performance of a modified samples change with varying processing conditions?

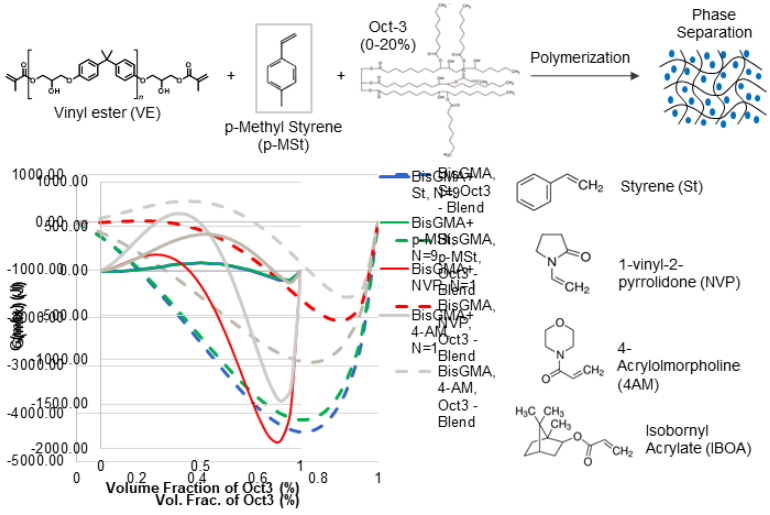
Curing behavior of photolithography resins – neat and modified



Does the addition of a liquid rubber modifier alter the cure kinetics of a vinyl ester resin?

- **Cure kinetics of resins during print are similar to those of known vinyl ester-styrene resins cured with heat**
- **Overall reaction rates of both resins, modified and unmodified, are the same**
- **Both achieve the same extent of reaction**
  Differences in material properties, such as modulus or T_g, are not a result of disparities in conversion
- **All samples post cured to achieve similar, maximum, conversions**

Thermodynamic model – revisited III



4. Graduate Presentations

APPROVED FOR PUBLIC RELEASE

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Artificial Noise-Aided MIMO Authentication via Fingerprint Embedding

Jake B. Perazzone	Dr. Paul Yu	Dr. Brian Sadler	Dr. Eric Graves	Prof. Rick Blum
Graduate Student	Mentor	Mentor	Mentor	Adviser
Lehigh University	ARL CISD	ARL VTD	ARL CISD	Lehigh University

6 August 2020

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

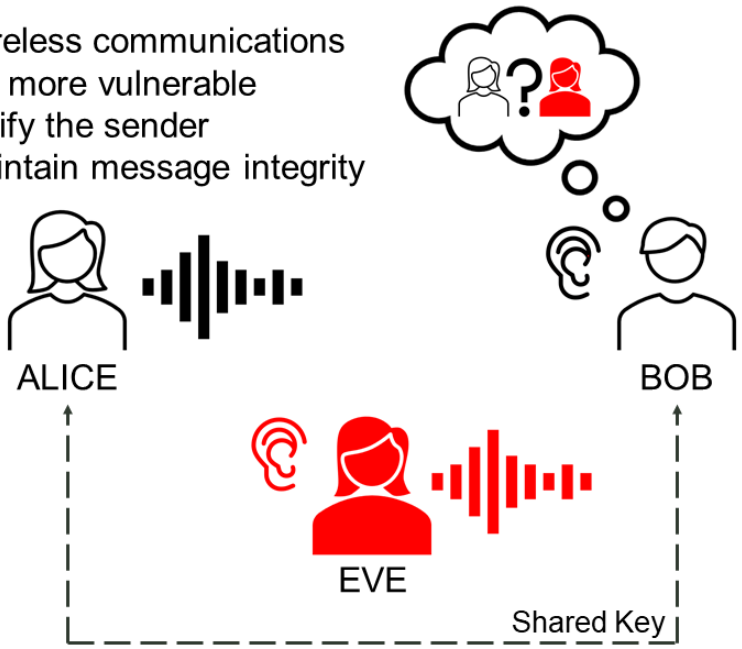
SECURE COMMUNICATION IN CONTESTED ENVIRONMENTS



APPROVED FOR PUBLIC RELEASE

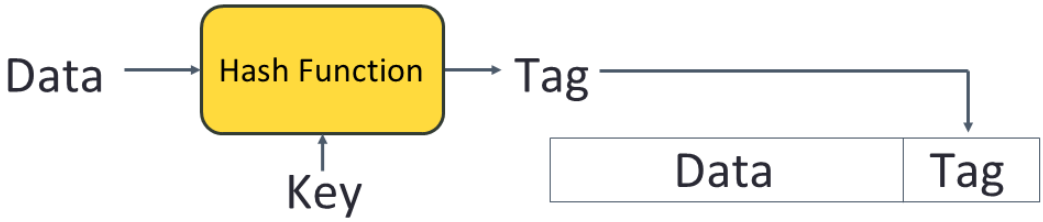
AUTHENTICATION OVERVIEW

- Wireless communications are more vulnerable
- Verify the sender
- Maintain message integrity



HASH-BASED MESSAGE AUTHENTICATION

- **Cryptographic protocol: "Hash-Based Message Authentication Codes"**



- **What if Eve can easily invert the hash function?**
  - We protect the key by hiding the tag

FINGERPRINT EMBEDDING AT THE PHYSICAL LAYER

- **Append**



- **Superimpose**



APPROVED FOR PUBLIC RELEASE

MIMO AND ARTIFICIAL NOISE

Multiantenna (MIMO) Beamforming



MIMO AND ARTIFICIAL NOISE

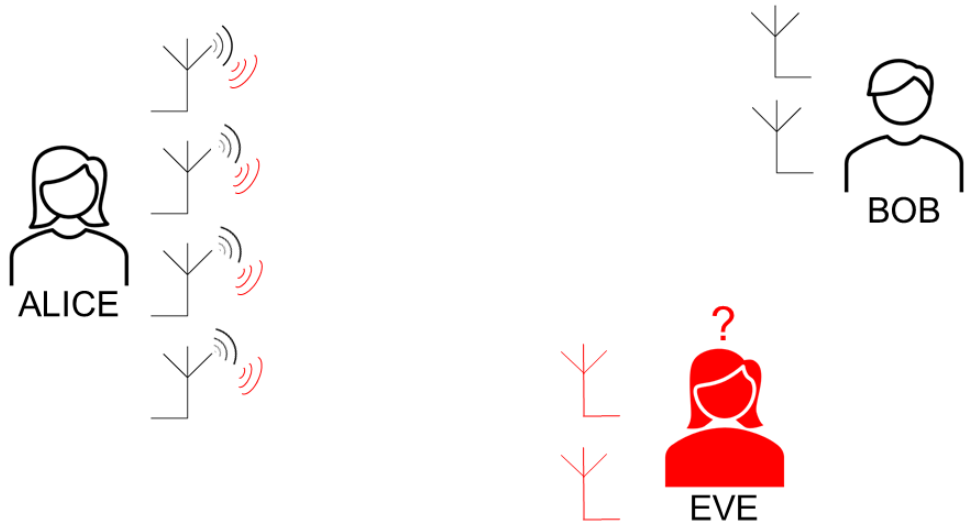
Multiantenna (MIMO) Beamforming



APPROVED FOR PUBLIC RELEASE

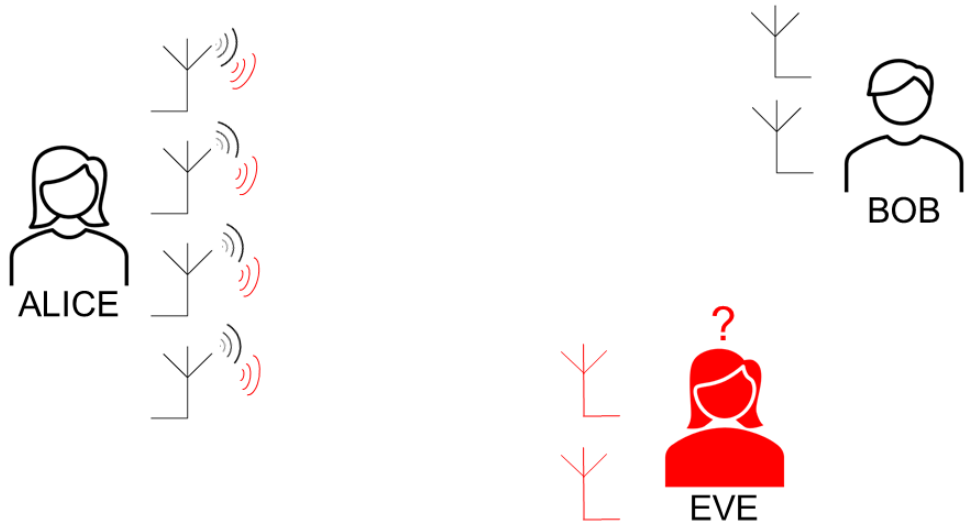
MIMO AND ARTIFICIAL NOISE

Artificial Noise



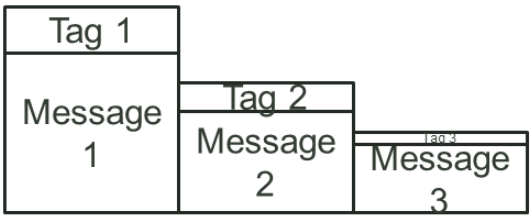
MIMO AND ARTIFICIAL NOISE

Channel Estimation Error

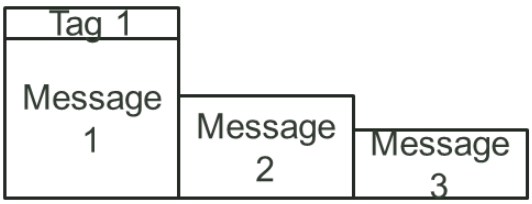


TAG EMBEDDING STRATEGY

- **All Modes (AM)**



- **Strongest Mode Only (SM)**

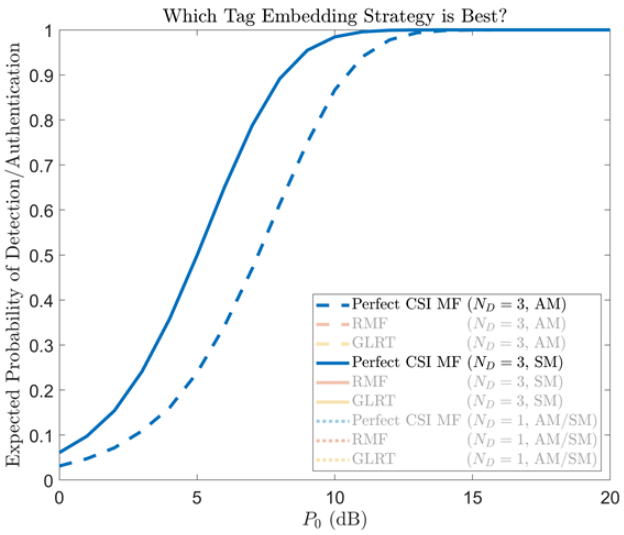


OBJECTIVES

1. **Make Bob's detection/authentication problem robust to channel estimation errors and resulting residual AN**
   - Determine best tag embedding procedure
   - Is AN still advantageous?

2. **Assess Eve's ability to optimally recover the key from observations**
   - Eve knows everything about the system except the key
   - Allows Alice and Bob to plan when to rekey

BOB DETECTION/AUTHENTICATION PERFORMANCE



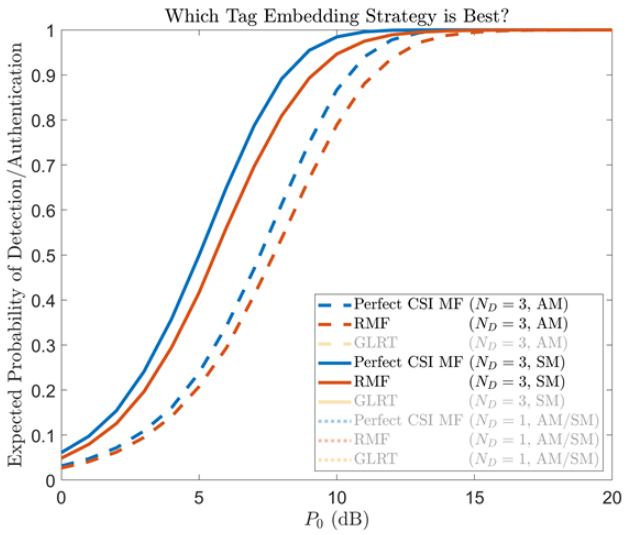
2 Tag Embedding Strategies

1. Embed on all "modes" (AM) - - - - - - - -
2. Embed on strongest mode (SM) _____

3 Tests

1. Matched Filter (with perfect CSI)

BOB DETECTION/AUTHENTICATION PERFORMANCE



2 Tag Embedding Strategies

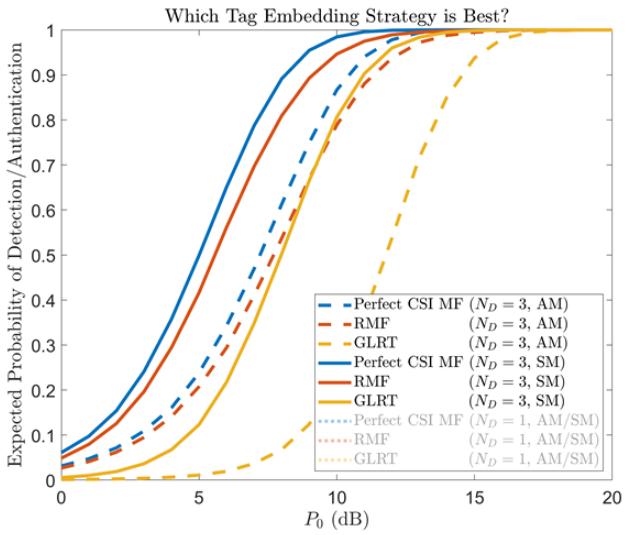
1. Embed on all "modes" (AM) - - - - - - - -
2. Embed on strongest mode (SM) _____

3 Tests

1. Matched Filter (with perfect CSI)
2. Robust Matched Filter (with imperfect CSI)

UNCLASSIFIED

BOB DETECTION/AUTHENTICATION PERFORMANCE



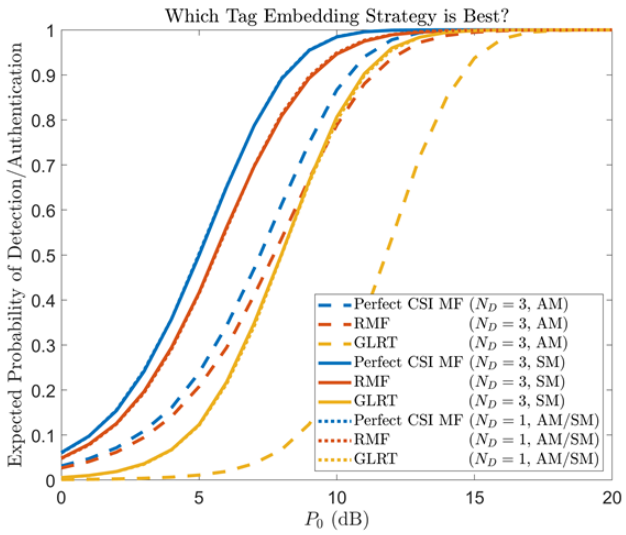
2 Tag Embedding Strategies

1. Embed on all "modes" (AM) - - - - - - - -
2. Embed on strongest mode (SM) _____

3 Tests

1. Matched Filter (with perfect CSI)
2. Robust Matched Filter (with imperfect CSI)
3. GLRT

BOB DETECTION/AUTHENTICATION PERFORMANCE

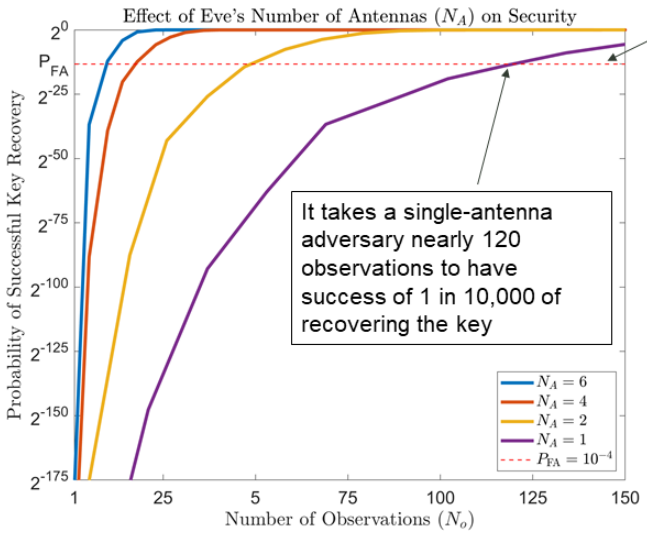


Takeaways

1) Single mode only embedding strategy has better performance

2) Transmitting AN in more dimension does not affect Bob (but will affect Eve)

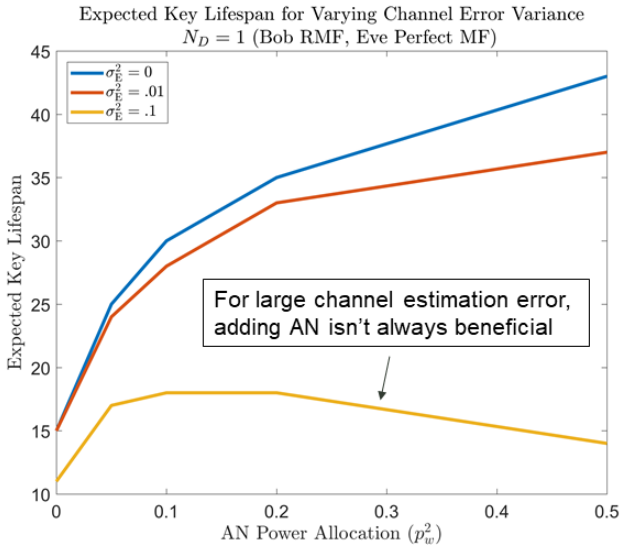
AUTHENTICATION SECURITY



Guaranteed Security Level

- Key lifespan: Number of times key can be used before it's deemed too vulnerable
- Must be careful when planning to rekey

AUTHENTICATION SECURITY



- Key lifespan: Number of times key can be used before it's deemed too vulnerable
- Artificial noise impacts Bob to severely to increase security

SUMMARY

- **We have designed and analyzed a framework for/with**
  - Highly secure network authentication via multiple antennas
  - Sustained key secrecy via artificial noise
  - Robust operation via signal processing

- **Publications**
  - J. B. Perazzone, P. L. Yu, B. M. Sadler, and R. S. Blum, "Artificial Noise-Aided Physical Layer Authentication with Imperfect CSI," *IEEE Transactions on Information Forensics and Security*, submitted, 2020.
  - J. B. Perazzone, P. L. Yu, B. M. Sadler, and R. S. Blum, "Authenticated Side-Channel via Fingerprint Embedding Min-Entropy Analysis," *IEEE Commun. Lett.*, in preparation, 2020.

APPROVED FOR PUBLIC RELEASE

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Artificial Noise-Aided MIMO Authentication via Fingerprint Embedding

THANK YOU!

Jake B. Perazzone	Dr. Paul Yu	Dr. Brian Sadler	Dr. Eric Graves
Graduate Student	Mentor	Mentor	Mentor
Lehigh University	ARL CISD	ARL VTD	ARL CISD

24 July 2020

APPROVED FOR PUBLIC RELEASE
APPROVED FOR PUBLIC RELEASE



APPROVED FOR PUBLIC RELEASE

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

The Influence of Dynamic Visual Scene Statistics on Pupil Size

Peter Hanson
Graduate Student, University of Texas, El Paso
Research Intern, ARL West

DISTRIBUTION STATEMENT GOES HERE

28 07 2020

APPROVED FOR PUBLIC RELEASE
APPROVED FOR PUBLIC RELEASE

ARMY RELEVANCE

- **Human Agent Teaming (HAT) Essential Research Program**
  - We want to understand how we can leverage a common physiological sensor (eye tracking) to predict mental states while soldiers are engaged in realistic tasks (free navigation) within a complex environment or real-world operation.
  - We believe pupillometry can serve as a useful and effective data source for adaptive future technologies, specifically, in predicting mental states related to arousal, mental load, stress and attention (Cohen Hoffing & Thurman, 2020).





Hoffing, R. A. C., Thurman, S. M. (2020). The State of the Pupil: Moving Toward Enabling Real-World Use of Pupillometry-Based Estimation of Human States. **ARL-TR-8947.**

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

BACKGROUND

- **We know that pupil size is influenced by cognitive factors (mental workload, attention, decision making)** (Cohen Hoffing et al., 2020)
- **However, pupil size is also influenced by *non-cognitive* factors (luminance, vergence)** (for review see Mathot, 2018).
- **This project aims to develop better models to account for luminance-based changes in pupil size while subjects navigate a complex 3D virtual environment.**
- **Hypothesis: If we can better account for *non-cognitive* influences, then it will help us to factor these out to improve estimation of cognitive-linked pupil response for real-world applications.**

Hoffing, R. A. C., Lauharatanahirun, N., Forster, D. E., Garcia, J. O., Vettel, J. M., & Thurman, S. M. (2020). Dissociable mappings of tonic and phasic pupillary features onto cognitive processes involved in mental arithmetic. ***PloS one***, *15*(3), e0230517.
Mathôt, S. (2018). Pupillometry: Psychology, physiology, and function. ***Journal of Cognition***, *1*(1).

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

HUMAN INTEREST DETECTOR (HID) EXPERIMENT

- **35 subjects**
- **TASK: Navigate a virtual environment and search for target objects (i.e. Helicopters, humvees, etc).**
  - Used mouse and keyboard to navigate
  - Total duration was about 12 minutes
  - Collected eye tracking: gaze position and pupil size



Navigation task:
Identify targets and keep a mental count

RESEARCH QUESTION: How well do RGB pixel intensities explain variations in pupil size?

APPROACH: Examine the inter-relationship between RGB scene statistics, luminance measurements, and pupil dynamics over time

APPROVED FOR PUBLIC RELEASE

OVERALL PROJECT GOALS

1. **Generate a sequence of "snapshots" for each subject by using software to replay their session (post-hoc), and then saving images**

2. **Use a photospectrometer to collect data from the laboratory to convert RGB intensities to units of luminance (cd/m^2)**

3. **Model the relationship between variations in luminance and the expected change in pupil size (**Korn & Bach, 2016**)**

4. **Analyze how RGB intensities influence pupil size using 2 approaches**

   a. **Foveal Windows approach**
   b. **Pixel-by-pixel correlation maps**



Korn, C. W., & Bach, D. R. (2016). A solid frame for the window on cognition: Modeling event-related pupil responses. ***Journal of Vision***, *16*(3), 28-28.

APPROVED FOR PUBLIC RELEASE

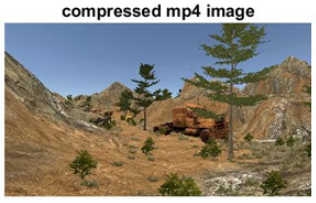
CREATING AND STORING SNAPSHOTS

- **Each subject had ~80k snapshots (png images) taking up 200gb**
- **To reduce storage space (to ~2gb), we used mp4 video compression**
- **We compared mp4 images to the original png images to ensure this didn't introduce too many artifacts**

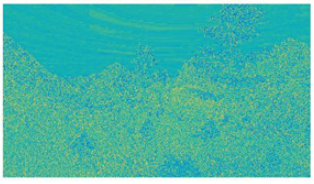
png image



compressed mp4 image



99.8% within 5% delta

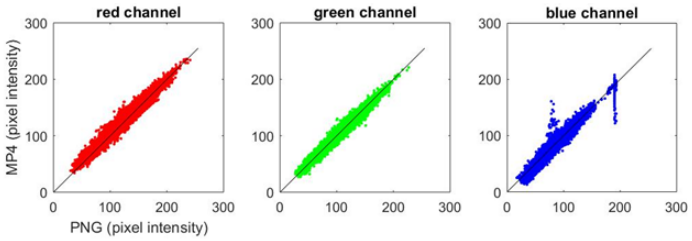


Bland Altman analysis

RED
bias = 0.7
95% COR= 12.1

GREEN
bias = -0.8
95% COR = 8.0

BLUE
bias = -0.4
95% COR = 13.6

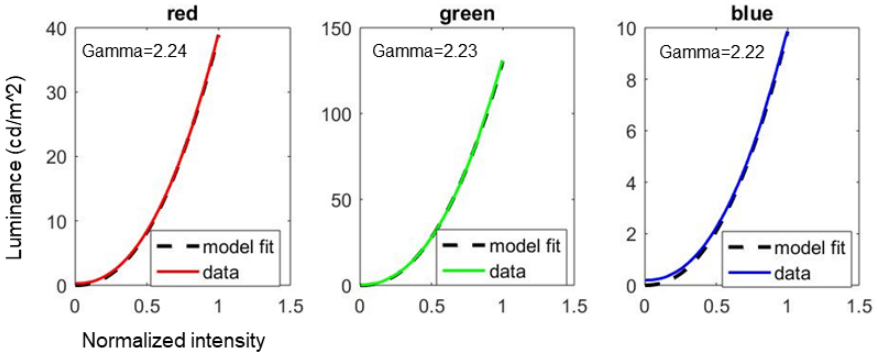


APPROVED FOR PUBLIC RELEASE

CONVERTING RGB TO LUMINANCE

- **We used a photospectrometer to measure luminance across the entire range from 0 (min) to 255 (max) for each color channel seperately**

- **We fit the data with an exponential function to derive a gamma parameter that non-linearly maps RGB intensities to luminance space**
  - E.g. this is the typical procedure for gamma-correcting a monitor



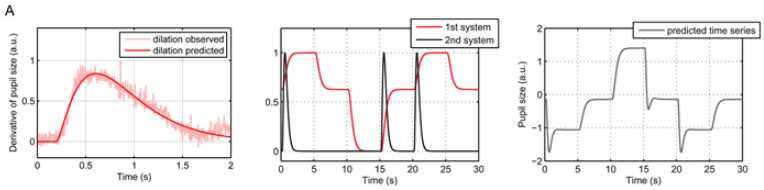
APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

PUPILLARY LIGHT RESPONSE (PLR) MODEL

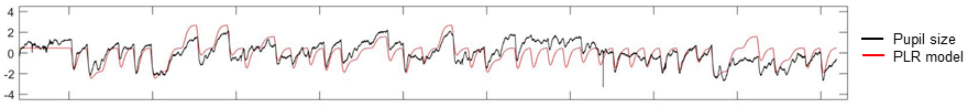
- **We modeled the pupil light response as a function of luminance dynamics using a classic approach of convolving with a gamma pdf**
  - accounts for sluggishness and canonical shape of pupil light response

- **As suggested by Korn & Bach (2016), we separately model the rapid constrictions resulting from sudden luminance increases (2nd system)**



IMAGES FROM: Korn, C. W., & Bach, D. R. (2016). A solid frame for the window on cognition: Modeling event-related pupil responses. ***Journal of Vision***, *16*(3), 28-28.

- **E.g. this model has fit well to data in our lab using a very simple task**

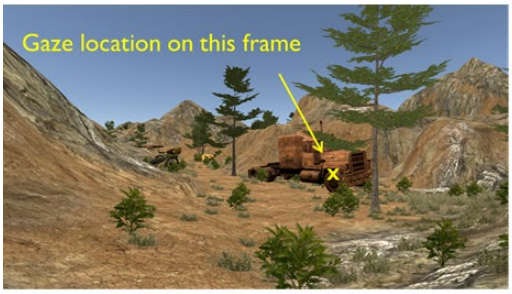


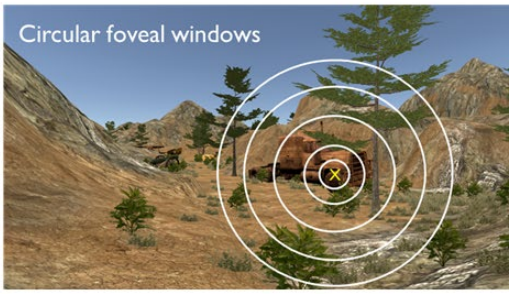
APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

FOVEAL WINDOWS APPROACH

- In this approach we took different sized windows to see how mean luminance in R, G, B channels affects the subject's pupil size.
- Sizes of windows: 50, 150, 300, 500, 700 pixels, and "Full Frame"
- We first applied PLR model to mean luminance, then examined the correlation with pupil as a function of window size



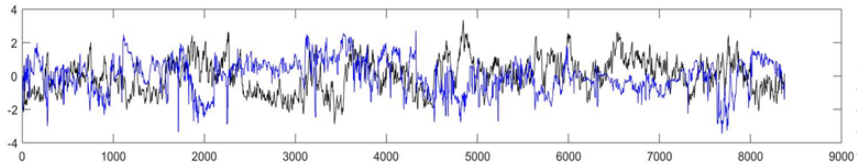


APPROVED FOR PUBLIC RELEASE

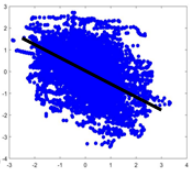
APPROVED FOR PUBLIC RELEASE

ANALYSIS: CORRELATION COEFFICIENTS

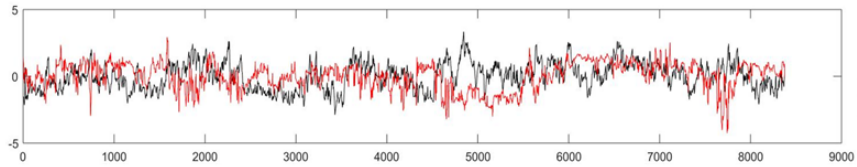
Example: Blue channel 700 pixel window size

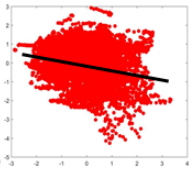


scatterplot



Example: Red channel 700 pixel window size



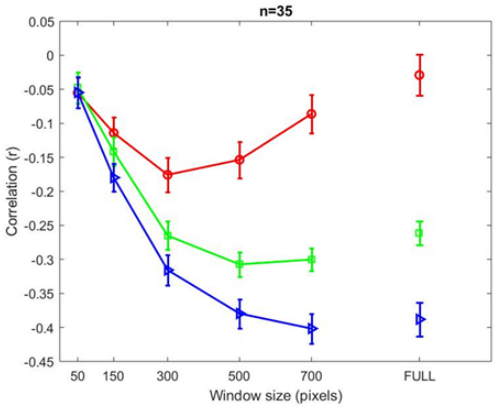


APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

GROUP RESULTS

- **Blue channel was most strongly negatively correlated**
  - Larger windows (700+ pixels) had strongest relationship
  - Green channel followed a similar pattern
- **Red channel least strongly correlated**
  - Intermediate windows (300 pixels) had strongest relationship



APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

PIXEL-BY-PIXEL CORRELATION MAPS

- **The foveal window approach makes the assumption that ALL pixels near fixation contribute EQUALLY to pupil size fluctuations**
- **Using a pixel-by-pixel approach, we can assess if this is true or not.**
- **If not true, then we can DISCOVER more detailed spatial maps of how pixels near fixation actually influence pupil size.**

e.g. lower contribution outside the foveal window



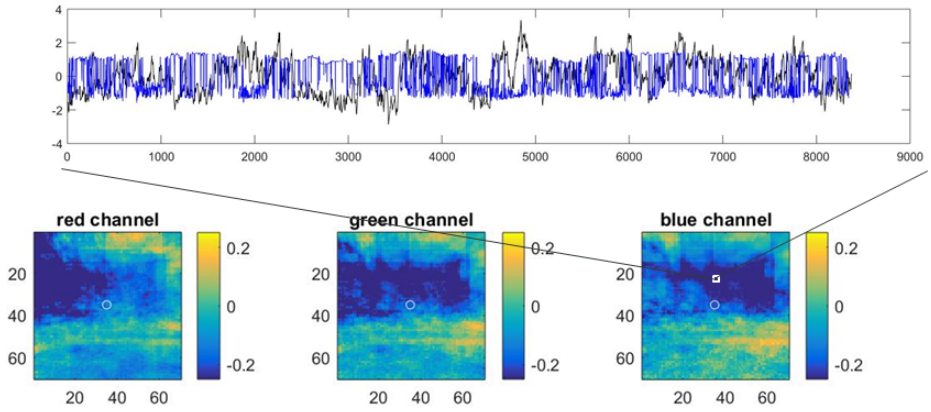
Assumes equal contribution within the circular foveal window

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

EXAMPLE CORRELATION MAP RESULTS

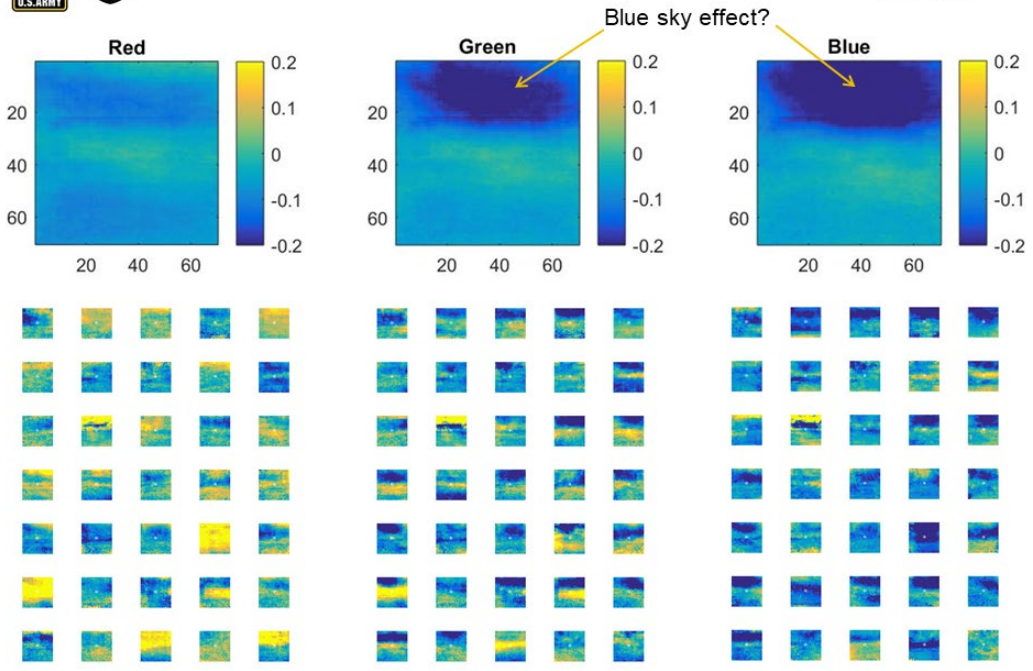
- Correlation maps for a single example subject
- Inset shows time series for one pixel in the blue channel



APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

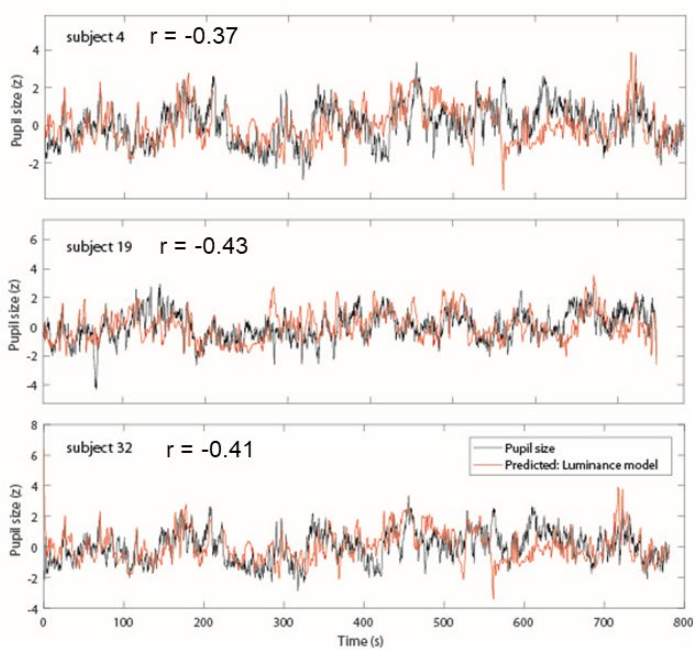
GROUP MAPS (INDIVIDUAL SUBJECTS BELOW)



APPROVED FOR PUBLIC RELEASE

ABILITY TO PREDICT PUPIL SIZE

- **Some examples showing how well this model of RGB statisitics can predict pupil size:**



CONCLUSIONS

- **There is a strong negative correlation between pupil size and the intensity of RGB scene statistics**
- **Based on the results from the foveal window approach we can conclude that when it comes to window sizes:**
  - Larger window sizes better capture influence of blue and green channels
  - Intermediate window sizes better captures the influence of the red channel
- **Based on the results from the pixel-by-pixel approach we can conclude that for the green and blue pixel channels:**
  - The strongest correlation is for pixels just above the point of gaze
  - We hypothesize this is a result of the blue sky in this task environment
- **Overall the results have helped in our understanding of how scene statistics should be analyzed in complex scenes to best predict pupil size fluctuations caused by light.**

FUTURE WORK

- **We wonder if these results would generalize to real-world images or other environments, or is the hypothesized "blue sky" effect specific to this task?**
- **Can we use this new knowledge to develop a better model of pupil changes from scene statistics in this task, and thereby improve our ability to estimate cognitive effects (e.g. Target detections)?**
- **How do other scene statistics interact with RGB intensity to influence on pupil size?**
  - The properties (specifically) of fixated objects vs. other scene elements
  - Global level of environmental brightness / darkness

APPROVED FOR PUBLIC RELEASE



APPROVED FOR PUBLIC RELEASE

U.S. ARMY COMBAT CAPABILITIES DEVELOPMENT COMMAND – ARMY RESEARCH LABORATORY

Study of Thermal and Vibrational Properties of Terminated Diamond Surfaces from First Principle Calculations

Erick Guzman

Graduate Student @ California State University Northridge

Mentor: Dr. Mahesh R. Neupane

RF and Logic ICs Branch, Advanced Electronics Division

DISTRIBUTION STATEMENT GOES HERE

07 15 2020

APPROVED FOR PUBLIC RELEASE

APPROVED FOR PUBLIC RELEASE

BACKGROUND INFO

- **Physics B.S. from California State University Northridge (2017)**
- **Physics M.S. from CSUN (2020)**
- **Research Focus is Computational Materials Science**
- **Returning student from 2019 Summer Internship**
- **Attending UC Riverside Electrical Engineering PhD program in the Fall**



APPROVED FOR PUBLIC RELEASE

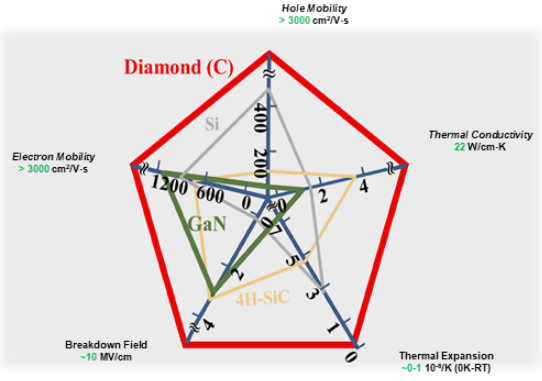
OUTLINE

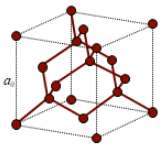
- What are the benefits of Diamond as a Semiconductor? And why would this material be useful?
- What are we looking for when analyzing thermal and vibrational data?
- What are our objectives and how did we realize them?
- How do we know our data is accurate and why is it important?
- What are the next steps in this work?

APPROVED FOR PUBLIC RELEASE

BACKGROUND

- Diamond is an attractive semiconductor with properties such as:
  - High electron/hole mobility
  - Thermal Conductivity
  - Surface power density





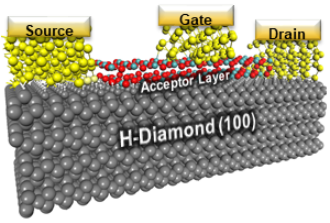
Diamond unit cell

- Diamond has good balance of:
  - Low *dielectric constant* (5.5)
  - High *saturation velocity* (~1x10^7 cm/s for holes)

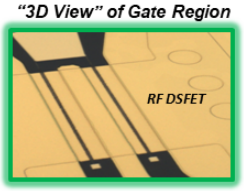
Diamond consistently outperforms competing ultra-wide band gap (UWBG) material systems for high-field, high-temperature device applications

MOTIVATION

- **In-house Surface Field Effect (SFET) device performance limited by surface vibrational & thermal properties**



"3D View" of Gate Region



L_g = 0.10 um
W_g = 40 um

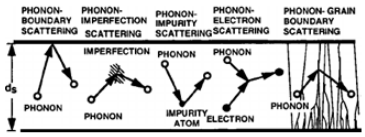
Surface structural and vibrational properties influence device parameters such as carrier mobilities, saturation velocity and carrier concenteration

- **Limited theoretical/modeling on the fundamental properties, such as Phonon Dispersion, Raman Spectra, and Thermal Conductivity**
- **Predictive modeling could help us make informed decisions on surface types for the desired device performance.**

Impact to the Army: Scaled RF devices with superior thermal management and operational frequencies for Radar Applications- consistent with one of the Army's modernization priorities (RF Materials)

BACKGROUND

- **Phonon frequencies describe the movement of atoms in the structure**

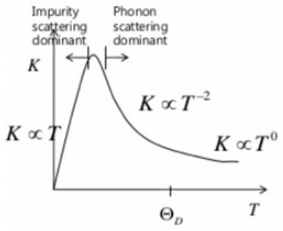


- **Higher Optical Phonon Frequency (E_{opt}) -> High Saturation Velocity (V_s) in Diamond FET**
  - At high electric fields, electrons lose energy by optical phonon emission.
  - This process governs the saturation of carrier velocities in steady state (DC, or direct current) transport, and velocity overshoot in non-equilibrium situations.

$$v_s = \sqrt{\frac{8E_{opt}}{3\pi m^*}\tanh(E_{opt}/2kT)}$$

- **Thermal conductivity depends on atomic mass and bond lengths**

Temperature Dependence of Thermal Conductivity



- **Thermal conductivity is directly related to device failure under high temperature environment**
  - Phonon-boundary scattering
  - Phonon-defect scattering

OBJECTIVES

- To validate developed and models and predicted vibrational properties against experimental data
- To analyze the effects of termination on diamond surfaces on
  - ✓ Maximum Optical Frequencies
  - ✓ Peak movement
  - ✓ Optical and acoustic modes
- To validate developed and models and predicted thermal conductivity (TC) for the bulk diamond system against experimental data
- To analyze the effect surface formation and termination on TC
- To find correlation between vibrational and thermal data

APPROVED FOR PUBLIC RELEASE

METHODS/TOOLS

- **Modified VASP code** (Created by Dr. Zhang at CSUN)
  - Used to relax starting structure to optimal state using conjugate gradient method
  - Used to simulate Raman Spectra
    - Combine force calculation done within Density Functional Theory (DFT) and polarizability derivatives
- **Phonopy** [1]- a PYTHON based tool
  - Used to perform phonon calculations and outputs Phonon Dispersion and Phonon Density of States (PDOS)
- **ShengBTE** [2]
  - Used to calculate specific heat and thermal conductivity (TC) by solving the Boltzmann Transport equation (BTE)
    - Takes 2nd order forces output from Phonopy
    - Takes 3rd order forces output created from multiple DFT based structural relaxations

Kohn-Sham equation for Total Energy of a many body system

$$E=\sum_i \varepsilon_i-\frac{1}{2}\int\int\frac{n(\vec{r})n(\vec{r}')}{|\vec{r}-\vec{r}'|}d^3rd^3r'+\int n(\vec{r})\{\varepsilon_{xc}[n(\vec{r})]-\mu_{xc}[n(\vec{r})]\}d^3r$$

Force Constant Matrix

$$\Phi_{\alpha\beta}(il,jl')=\frac{\partial^2 E}{\partial r_\alpha(l)\partial r_\beta(l')}=-\frac{\partial F_\alpha(il)}{\partial r_\beta(jl')}$$

Dynamical Matrix

$$D_{\alpha\beta}(i,j,\mathbf{q})=\frac{1}{\sqrt{m_i m_j}}\sum_{l'}\Phi_{\alpha\beta}(i0,jl')\exp[i\mathbf{q}.(\mathbf{r}(jl')-\mathbf{r}(i0))]$$

After diagonalisation: $e(\mathbf{q}).\Omega(\mathbf{q})=D(\mathbf{q}).e(\mathbf{q})$

$$e(\mathbf{q},\lambda)=\begin{bmatrix}\sqrt{m_1}r_x(1,\mathbf{q},\lambda)\\ \sqrt{m_1}r_y(1,\mathbf{q},\lambda)\\ \sqrt{m_1}r_z(1,\mathbf{q},\lambda)\\ \vdots\\ \sqrt{m_N}r_z(N,\mathbf{q},\lambda)\end{bmatrix}\quad \Omega(\mathbf{q})=\begin{bmatrix}\omega(\lambda_1,\mathbf{q}) & . & . & . & .\\ . & \omega(\lambda_2,\mathbf{q}) & . & . & .\\ . & . & \omega(\lambda_3,\mathbf{q}) & . & .\\ . & . & . & \ddots & .\\ . & . & . & . & \omega(\lambda_{3N},\mathbf{q})\end{bmatrix}$$

$$D(\mathbf{q})=\begin{bmatrix}D_{xx}(1,1,\mathbf{q}) & D_{xy}(1,1,\mathbf{q}) & D_{xz}(1,1,\mathbf{q}) & \dots & D_{xz}(1,N,\mathbf{q})\\ D_{yx}(1,1,\mathbf{q}) & D_{yy}(1,1,\mathbf{q}) & D_{yz}(1,1,\mathbf{q}) & \dots & D_{yz}(1,N,\mathbf{q})\\ D_{zx}(1,1,\mathbf{q}) & D_{zy}(1,1,\mathbf{q}) & D_{zz}(1,1,\mathbf{q}) & \dots & D_{zx}(1,N,\mathbf{q})\\ \vdots & \vdots & \vdots & \ddots & \vdots\\ D_{xx}(N,1,\mathbf{q}) & D_{xy}(N,1,q) & D_{xz}(N,1,\mathbf{q}) & \dots & D_{xz}(N,N,\mathbf{q})\end{bmatrix}$$

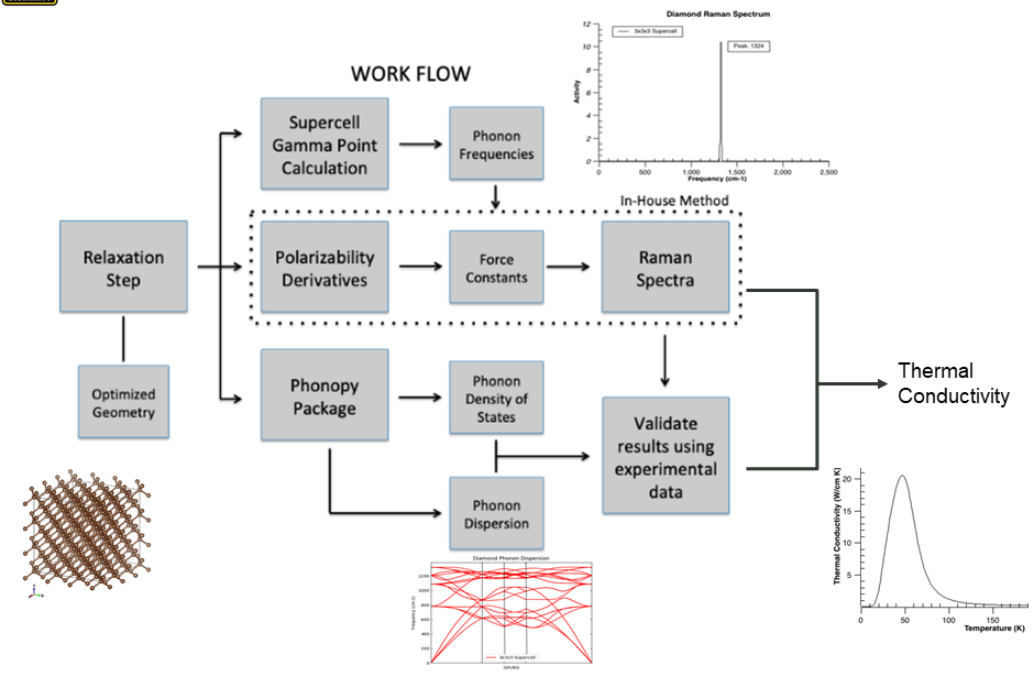
Lattice Thermal Conductivity

$$\kappa_{\alpha\beta}=\frac{1}{V}\sum_{j,\vec{q}}\frac{\hbar^2}{k_B T}\omega_j(\vec{q})v_{j\alpha}(\vec{q})F_{j\beta}(\vec{q})\,n_j^0(\vec{q})[n_j^0(\vec{q})+1]$$

[1] Togo, A et al. Scr. Mater., 2015
[2] Wu Li, et al. Comp. Phys. Commun., 2014

APPROVED FOR PUBLIC RELEASE

SIMULATION WORK FLOW



APPROVED FOR PUBLIC RELEASE

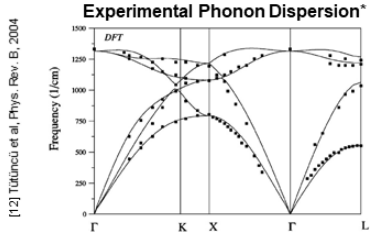
APPROVED FOR PUBLIC RELEASE

Results

APPROVED FOR PUBLIC RELEASE

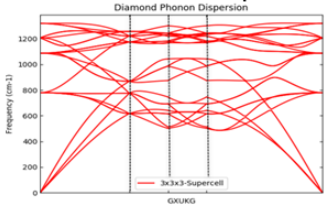
BULK DIAMOND- PHONON DISPERSION AND RAMAN SPECTRA

Experimental Phonon Dispersion*

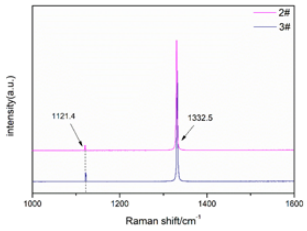


[12] Tütüncü et al, Phys. Rev. B, 2004

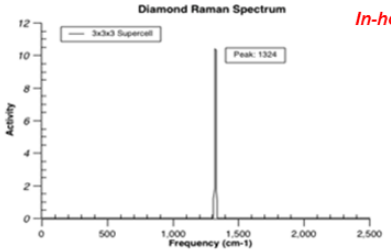
Predicted Phonon Dispersion



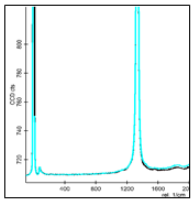
Predicted phonon dispersion feature matches well with the experimental (EELS) and theoretical (DFT) data



[3] Jinlong Liu, et al. DRM, 2020



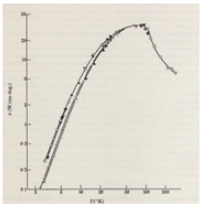
In-house Raman Measurement

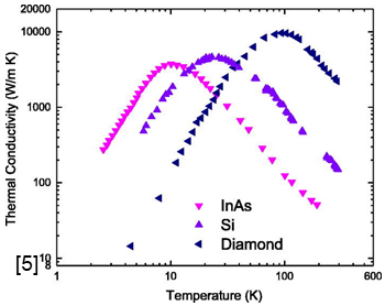


Raman spectra matches experiment within +/- 1% error

BULK DIAMOND EXPERIMENTAL VALIDATION

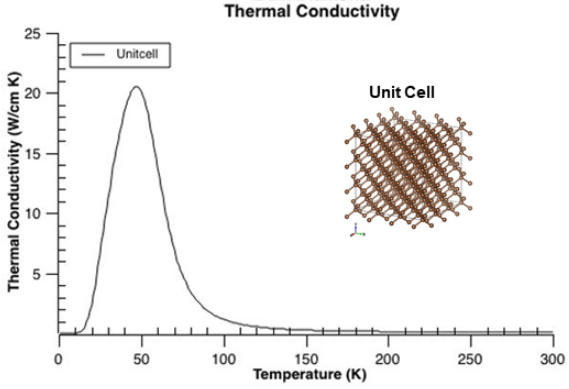
[4]





[5]

Bulk Diamond
Thermal Conductivity

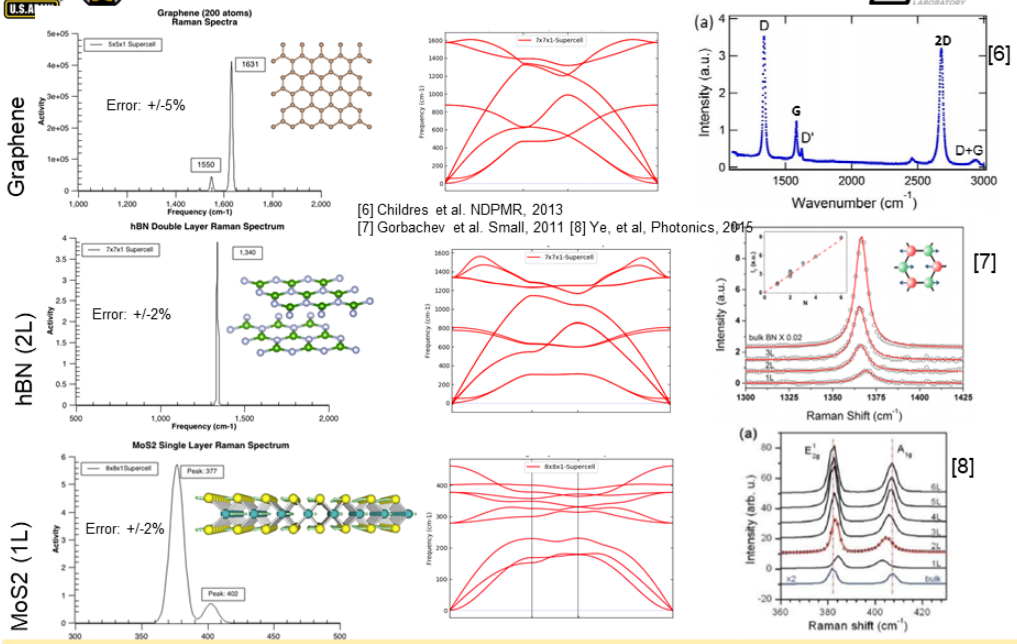


Unit Cell

Predicted Thermal Conductivity (TC) agrees well with experiment (±5% error)

[4] R. Berman, et al. Proc. R. Soc. Lond., 1997
[5] B. Sarkar, et al. *Journal of Applied Physics*, 2018

EXPERIMENTAL VALIDATION (CONT.)



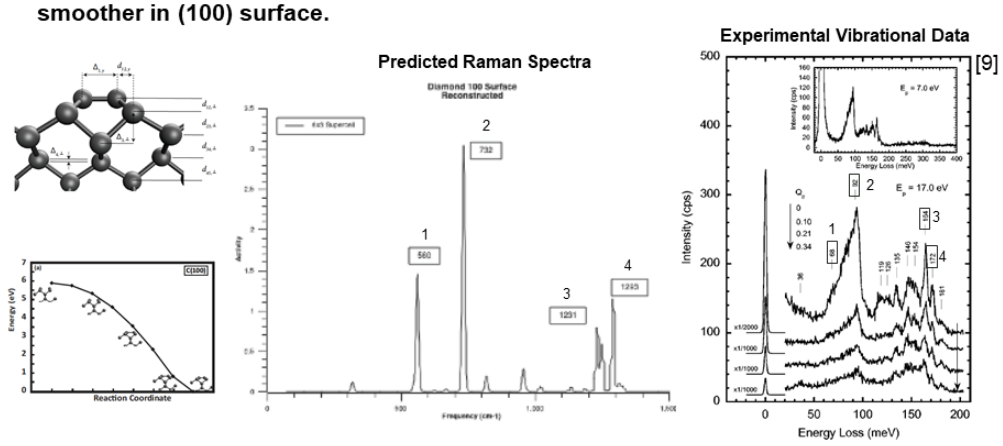
[6] Childres et al. NDPMR, 2013
[7] Gorbachev et al. Small, 2011 [8] Ye, et al, Photonics, 2015

Model/Method successfully predicts Raman and Phonon dispersion for monolayer (graphene), bilayer (hBN) and tetra-layer systems (MoS_2).

2X1 SURFACE

- **2X1 Diamond surface is stable surface and widely used.**
- **A parallel study [5] from our group about the 2x1 (100) reconstructed structure suggest that the transformation from the bulk to reconstructed phase is smoother in (100) surface.**

[5]



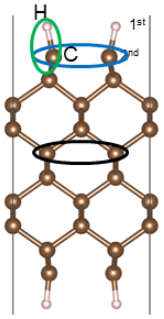
For all peaks in 2x1 Diamond (100) surface, the model predicts the Raman active peaks within 7% error

[5] Gomez, et al. (Under Review)
[9] Thachepan, et al, Phys. Rev. B, 2003

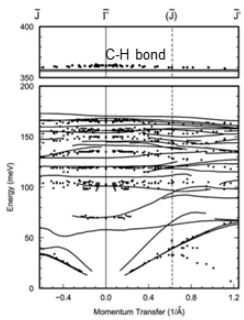
VIBRATIONAL DATA

H-Termination

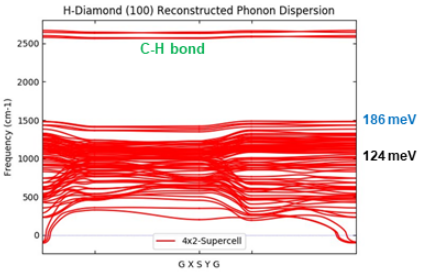
- **Phonon Dispersion**



(100)



[10]



Bond	Experiment	Actual
C-H (100)	1.09 Å	1.15 Å

- C=H bonds around 2500 cm^{-1} frequencies are caused by the symmetric and asymmetric stretch modes which are modeled correctly by our work

Highest optical phonon modes caused mainly by dimer stretch in the 1st layer of atoms with minor contributions coming from the 2nd and 3rd layer

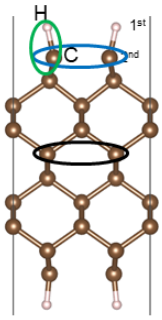
[10] Thachepan, Surachai et al. Phys. Rev. B 68. (2003).

APPROVED FOR PUBLIC RELEASE

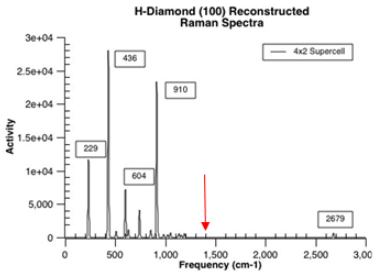
VIBRATIONAL DATA (CONT.)

H-Termination

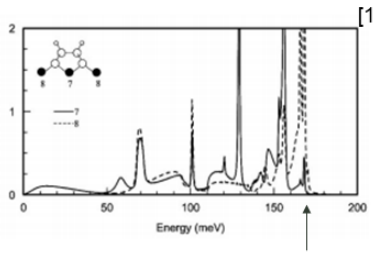
- **Raman Spectrum**



(100)



[10]



171 meV
(41.4 THz)

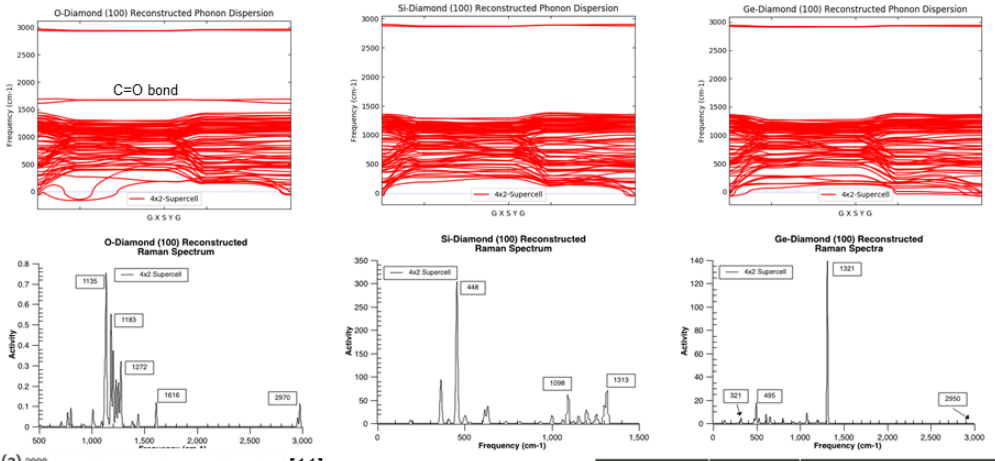
Structure	Surface	Frequency	
H-Diamond	(100)	1382 cm^{-1}	41.4 THz

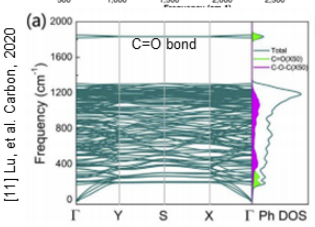
- Low Frequencies between 229 and 910 cm^{-1} (6.5 and 27 THz) caused by Hydrogen [PLEASE READ THE PAPER FURTHER- It appears everything is from C-H bonds Is it needed]
  - **1382 (41.4 THz) – Low activity diamond peak**
  - **2679 (80.3 THz) – Due to C-H bonds in the surface**

[10] Thachepan, Surachai et al. Phys. Rev. B 68. (2003).

COMPARISON OF RAMAN AND PHONON DISPERSION

Guzman and Neupane (to be published)





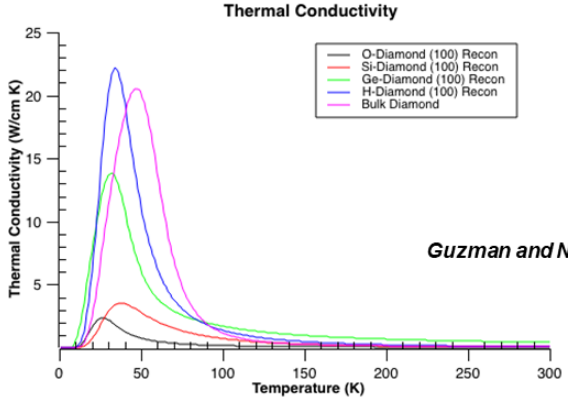
[11] Lu, et al. Carbon, 2020

[11]

Maximum optical frequency is modulated by surface termination

Structure	Surface	Frequency	
O-Diamond	(100)	1272 cm^{-1}	38.13 THz
Si-Diamond	(100)	1313 cm^{-1}	39.36 THz
Ge-Diamond	(100)	1321 cm^{-1}	39.60 THz

COMPARISON OF THERMAL CONDUCTIVITY



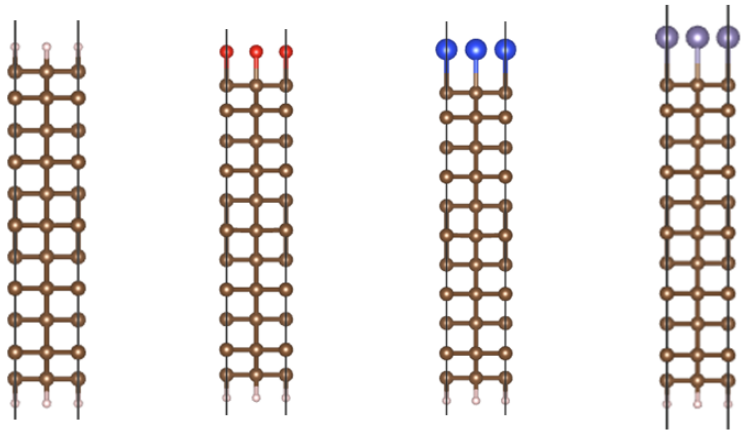
Guzman and Neupane (to be published)

- **TC for H-Diamond (100) is close to the TC of the bulk diamond system, but little variation is mainly due to structure induced phonon confinement.**
- **TC for H-Diamond (100) is consistently higher than Ge (1.6X), Si (6.2X), and O (8.8X)**
- **Harmonic forces and surface mass greatly influence thermal conductivity => Reduction in phonon group velocity**

- **These results are new and will be published soon.**

FUTURE WORK

- **Continue Vibrational and Thermal study of remaining (110) surfaces**
  - H-Diamond (110)
  - O-Diamond (110)
  - Si-Diamond (110)
  - Ge-Diamond (110)



APPROVED FOR PUBLIC RELEASE

SUMMARY

✓ **We successfully reproduced experimental phonon dispersion and thermal conductivity data for bulk diamond system**

✓ **We discovered new thermal conductivity findings related to Terminated surface structures**

✓ **Aside from the H-terminated surface , increase in thermal conductivity from O, Si, and Ge terminated structures related to increase in atom mass ->> Higher Mass, Lower Conduction**

✓ **Higher structure symmetry leads to higher thermal conductivity**

✓ ***We successfully, for the first time, demonstrated the use of surface terminates to modulate vibrational and thermal properties in diamond surfaces***

ACKNOWLEDGEMENTS

- Thank you to Dr. Neupane for his continuous support and guidance
- I appreciate the opportunity given to me by the DOD HBCU/MI Summer Internship Program

References

[1] Togo, A et al. "First principles phonon calculations in materials science". Scr. Mater. 108. (2015): 1–5.
[2] Wu Li, et al. "ShengBTE: a solver of the Boltzmann transport equation for phonons". Comp. Phys. Commun. 185. (2014): 1747–1758.
[3] Jinlong Liu, et al. "Carrier mobility enhancement on the H-terminated diamond surface". Diamond and Related Materials 104. (2020): 107750.
[4] R. Berman, Franz Eugen Simon and John Michael Ziman 1997 The thermal conductivity of diamond at low temperatures *Proc. R. Soc. Lond. A*220 171–183
[5] Gomez, Groves and Neupane, "Study of the structure-property Relationship in Diamond (100) and (111) Surfaces" (Under Review)
[6] Childres, I. et al. "Raman Spectroscopy of Graphene and Related Materials". New Developments in Photon and Materials Research. (2013): 403-418.
[7] Gorbachev, Roman V. et al. "Hunting for Monolayer Boron Nitride: Optical and Raman Signatures". Small 7. 4(2011): 465-468.
[8] Ye, M.; Winslow, D.; Zhang, D.; Pandey, R.; Yap, Y.K. Recent Advancement on the Optical Properties of Two-Dimensional Molybdenum Disulfide (MoS2) Thin Films. Photonics 2015, 2, 288-307.
[9] Thachepan, Surachai et al. "Surface vibrations of diamond C(001)(2 × 1)". Physical Review B - PHYS REV B 68. (2003).
[10] Thachepan, Surachai et al. "Surface phonons of C(001)(2× 1)-H". Phys. Rev. B 68. (2003).
[11] Shaohua Lu, Dong Fan, Chengke Chen, Yingshuang Mei, Yanming Ma, & Xiaojun Hu (2020). Ground-state structure of oxidized diamond (100) surface: An electronically nearly surface-free reconstruction Carbon, 159, 9 - 15.
[12] Tütüncü, H., \fi, S., & Srivastava, G. (2004). Structural, electronic, and dynamical properties of the C(001)-2x1 surface Phys. Rev. B, 70, 195401.

APPROVED FOR PUBLIC RELEASE

Citations

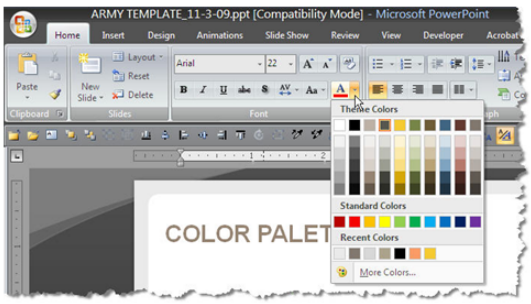
- [1] Togo, A et al. Scr. Mater., 2015
- [2] Wu Li, et al. Comp. Phys. Commun., 2014
- [3] Jinlong Liu, et al. DRM, 2020
- [4] R. Berman, et al. Proc. R. Soc. Lond., 1997
- [5] Gomez, et al. (Under Review)
- [6] Childres et al. NDPMR, 2013
- [7] Gorbachev et al. Small, 2011
- [8] Ye, et al. Photonics, 2015
- [9] Thachepan, et al. Phys. Rev. B, 2003
- [10] Thachepan, et al. Phys. Rev. B, 2003
- [11] Lu, et al. Carbon, 2020
- [12] Tütüncü et al, Phys. Rev. B, 2004

SLIDE TITLE GOES HERE

APPROVED FOR PUBLIC RELEASE

COLOR PALETTE

Each template has its own color palette. It is the top row of colors under the “Font Color,” “Shape Fill” and “Shape Outline” menus






Questions
?
?
Answers
?

1 (PDF)	DEFENSE TECHNICAL INFORMATION CTR DTIC OCA
1 (PDF)	DIR ARL RDRL DCL TECH LIB
2 (PDF)	DEVCOM ARL FCDD RLL PP P COLLINS D DIGGS