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### Influence of longer-range interactions on the computational self-assembly of crystal structures

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To effectively use the self-assembly of ordered structures to engineer new soft crystalline materials, we must understand how interactions between particles influence the structure that forms. Simulating self-assembled crystal structures using an isotropic pair potential is a promising way to systematically study this relationship. We designed a highly tunable two-well interaction potential and analyzed how adding a third attractive well affects what structures we observe. Adding a well resulted in an increase in coordination number from the original two-well structure. We also found that controlling longer-range interactions in this way decreases the diversity of structures observed. To determine whether these results are dependent on this particular interaction potential, we added a well to the Lennard-Jones Gauss (LJG) potential as well. The effect of adding a well to LJG must be studied further before conclusions can be made.

### I Introduction

The use of self-assembly in the design and synthesis of new materials with desirable properties is increasingly prevalent. It has been shown that soft matter building blocks such as metallic nanoparticles [1], micelles [2], and block copolymers [3, 4] can self-assemble into a diverse set of crystal structures. These building blocks are highly tunable, and because they are not subject to the constraints of chemical bonding, they can also self-assemble into structures without atomic equivalents [5, 6].

Previous work has shown that a variety of complex crystal structures can be observed in simulation using an isotropic interaction potential. A potential that has been widely used is the Lennard-Jones (LJ) potential, which forms face-centered cubic (fcc) structures for large clusters [7]. The one-well LJ potential can be combined with one Gaussian function to create the Lennard-Jones–Gauss (LJG) potential. Adding these longer-range interactions results in a wider variety of structures. Dshemuchadse *et al.* searched the phase spaces of the LJG potential and the oscillating pair potential and found 16 known crystal structures and 15 previously unknown ones [5].

Understanding how the properties of the interaction potential influence which crystal structures form can aid in the discovery and design of soft crystalline materials. In this work, we analyze how the structure we observe changes with the addition of an attractive well. By adding a well, we control longer-range interactions and add a competing length scale and force to the system. We design a two-well interaction potential made up of a soft potential function and three Gaussian functions and add a third well be adding two Gaussian functions. This potential is advantageous because it is more tunable than the LJG potential. We then add a well to select state points of the LJG potential with known structures found by Dshemuchadse *et al.* [5].

#### II Methods

The two-well interaction potential is the sum of a soft sphere potential and three Gaussian functions with alternating signs (SG3) (see Figure 1a):

$$V_{\rm SG3}(r) = \frac{1}{r^{12}} + \sum_{i=1}^{3} (-1)^{i} \varepsilon_{i} \exp\left[\frac{(r-\mu_{i})^{2}}{-2\sigma_{i}^{2}}\right].$$
 (1)

The first term is the soft sphere potential, which models the pair potential of soft spheres separated by a distance r. The second term is a summation of three Gaussian functions. The first Gaussian corresponds to the first well, the second with the hump between the wells, and the third with the second well. The parameters  $\varepsilon_i$ ,  $\mu_i$ , and  $\sigma_i$  control the height, position, and width of the three extrema, respectively. We arbitrarily set  $\varepsilon_1 = 5$ and  $\mu_1 = 1$ . The parameters  $\varepsilon_2$ ,  $\varepsilon_3$ , and  $\mu_3$  are varied. The location of the hump  $\mu_2$  depends on  $\mu_3$  so that the hump is halfway between the two wells. The widths of all Gaussians depend on  $\mu_3$  where

$$\sigma_1 = (\mu_2 - \mu_1)^2$$
$$\sigma_2 = \left(\frac{\mu_3 - \mu_1}{2}\right)^2$$
$$\sigma_3 = \frac{\sigma_1 + \sigma_2}{2}.$$

We construct the three-well interaction potential SG5 (see Figure 1b) by adding one positive and one negative Gaussian to Equation 1:

$$V_{\rm SG5}(r) = \frac{1}{r^{12}} + \sum_{i=1}^{5} (-1)^i \varepsilon_i \exp\left[\frac{(r-\mu_i)^2}{-2\sigma_i^2}\right].$$
 (2)

The parameters  $\varepsilon_i, \mu_i$ , and  $\sigma_i$  for  $1 \le i \le 3$  remain the same as those for the two-well potential. The location of the second hump  $\mu_4$  is set so the second hump is halfway between the second and third wells. The parameters  $\varepsilon_4, \varepsilon_5$ , and  $\mu_5$  are varied. The widths of the second hump and third well depend on  $\mu_5$  where

$$\sigma_4 = \left(\frac{\mu_5 - \mu_3}{2}\right)^2$$
  
$$\sigma_5 = (\mu_5 - \mu_4)^2.$$

We construct the LJG3 potential by adding two Gaussians to the LJG potential:

$$V_{\rm LJG3}(r) = \frac{1}{r^{12}} - \frac{2}{r^6} + \sum_{i=1}^3 (-1)^i \varepsilon_i \exp\left[\frac{(r-\mu_i)^2}{-2\sigma_i^2}\right].$$
 (3)

The parameter  $\sigma_1^2$  is set to 0.02 and the parameters  $\varepsilon_1$ and  $\mu_1$  are set to match state points with structures found by Dshemuchadse *et al.* [5]. The location of the second hump  $\mu_2$  is set so that it is located halfway between the second and third wells. The parameters  $\varepsilon_2$ ,  $\varepsilon_3$ , and  $\mu_3$  are varied. The widths of the second hump and third well depend on  $\mu_1$  and  $\mu_3$ :

$$\sigma_2 = \left(\frac{\mu_3 - \mu_1}{2}\right)^2$$
$$\sigma_3 = (\mu_3 - \mu_2)^2.$$

The LJG potential is a two-well potential, but the state points chosen from Dshemuchadse *et al.* consist of one well with a shoulder on the left side. Thus by adding a well, we are creating two-well potentials (see Figure 1c).



Figure 1: Interaction potential as function of interparticle distance r. (a) SG3 potential. The parameters varied are the height of hump ( $\varepsilon_2$ ), the depth of the second well ( $\varepsilon_3$ ), and the location of the second well ( $\mu_3$ ). (b) SG5 potential, created by the addition of a third well to SG3. The parameters varied are the height of the added hump ( $\varepsilon_4$ ), the depth of the added well ( $\varepsilon_4$ ), and the location of the added well ( $\mu_5$ ). (c) LJG3 potential, created by the addition of a well to LJG potential. The parameters varied are the height of hump ( $\varepsilon_2$ ), the depth of the second well ( $\varepsilon_3$ ), and the location of the second well ( $\mu_3$ ).

Molecular Dynamics (MD) simulations were performed in the NVT ensemble using the open-source simulation package HOOMD-blue [8, 9, 10]. Simulations of N = 4,096 particles were initialized on a regular grid in the gaseous phase. The initially high temperature was decreased linearly using a Nosé–Hoover thermostat over  $10^8$  time steps with a step size of  $d\tau = 0.005$ . Eventually, the particles condense into a liquid droplet and then solidify. The software *signac* was used for data management [11, 12].

The structures of the crystals formed in simulation are determined using *freud* [13]. First, we isolate a clean grain and determine its average coordination number (CN), the number of nearest neighbors of a given particle. This is done by plotting the radial distribution function (RDF), a histogram of the distances between every pair of particles, and computing the number of particles within the distance cuttoff after the first major peak of the RDF. We then use a bond-orientational order diagram (BOOD), which is a spherical representation of relative particle positions, to determine the directions of the lattice vectors that define the Bravais lattice. Next we determine the unit cell dimensions using cylindrical BOODs along these directions. We used Spglib to find the space group corresponding with the unit cell [14].

### III Results

The structures observed are reported an Table 1. The notation used is the Pearson Symbol, and structures with X as the prototypical structures do not have atomic equivalents.

The first round of SG3 simulations consisted of three phase diagrams varying each combination of the three

parameters. Eight crystal structures were observed (Figure 2a, c, e). The structure that formed generally depends on the location of the second well  $(\mu_3)$ . The height of the hump  $(\varepsilon_2)$  and the depth of the second well  $(\varepsilon_3)$  have little effect on the formed structure. Moving the second well to larger interparticle distances (increasing  $\mu_3$ ) increases the coordination number (Figure 2c, d).

Table 1: Pearson symbol, space group, coordination numbers CN, and average coordination number (CN) for each crystal structure observed.

Pearson Symbol	Space Group	$_{\rm CN}$	$\langle CN \rangle$
Known crystal structures			
cI16-X	$Ia\bar{3}d$	5	5
<i>cP</i> 1-Po	$P4_{1}32$	6	6
$tI4 ext{-Sn}$	$I4_1/amd$	14	14
$cP4 ext{-Li}$	$P4_{1}32$	6	6
hP1- $X$	P6/mmm	6	6
$hP1-Ca_{0.15}Sn_{0.85}$	P6/mmm	8	8
tI20- $X$	I4/mcm	9/10	9.2
$cF4 ext{-Cu}$	$Fm\bar{3}m$	12	12
$hP2 ext{-Mg}$	$P6_3/mmc$	12	12
tP30-CrFe	$P4_2/mnm$	12/14/15	13.5
cP8-Cr <sub>3</sub> Si	$Pm\bar{3}n$	12/14	13.5
$cI2 ext{-W}$	$Im\bar{3}m$	14	14
Previously unknown crystal structures			
tI10-X	I422	9	9
tP32- $X$	P4/ncc	14-19	15
oC64- $X$	Cmme	14-19	16
Aperiodic crystal structures and disorder			
octagonal quasicrystal	-	-	-
unidentified	-	-	-
disorder	-	-	-

We chose one two-well state point for each of tI20-X, cP4-Li, hP1-X, cF4-Cu, and tP30-CrFe from the phase diagrams shown in Figure 2. A hump and a well were added to each to create SG5 potentials (Figure 1b). For tI20-X, cP4-Li, hP1-X, and cF4-Cu, we first ran simulations with relatively small values for the height of the second hump  $(\varepsilon_4)$  and the depth of the third well  $(\varepsilon_5)$  (Figure 3). These phase diagrams show what happens as the second hump and third well are gradually added. The state points with  $\varepsilon_4 = \varepsilon_5 = 0$  are the original two-well state points. If we start with the tI20-X state point (Figure 3a) or the cP4-Li state point (Figure 3c), increasing  $\varepsilon_4$  causes the structure switch to tP30-CrFe and cP8-Cr<sub>3</sub>Si. If we start with the hP1-X state point (Figure 3e), increasing  $\varepsilon_4$  and  $\varepsilon_5$  causes the structure switch to hP2-Mg. Increasing  $\varepsilon_4$  further causes to structure to switch again to an octagonal quasicrystal. If we start with cF4-Cu (Figure 3g), the structure immediately becomes cI2-W and hP2-Mg with the addition of a second hump and third well. In this phase diagram, we also observe a structure that requires more advanced structure determination techniques to identify. For each of these original two-well structures, adding a second hump and third well causes a switch to a more highly coordinated structure (Figure 3b, d, f, h).

Next, we made the second hump and third well more pronounced, meaning that  $\varepsilon_4$  and  $\varepsilon_5$  are greater than 1. We varied the height of the second hump and the location of the third well to determine which structure is stable with the added third well. The tI20-X(Figure 4a) and cP4-Li (Figure 4b) two-well state points



Figure 2: Phase diagrams showing structures (top row) and coordination numbers (bottom row) of particles interacting *via* SG3 potentials. (a) Structures and (b) coordination numbers (CNs) for varying hump height ( $\epsilon_2$ ) and location of the second well ( $\mu_3$ ) for  $\varepsilon_3 = 2$ . (c) Structures and (d) CNs for varying the depth of the second well ( $\epsilon_3$ ) and location of the second well ( $\mu_3$ ) for  $\varepsilon_2 = 4$ . (e) Structures and (f) CNs for varying the hump height ( $\epsilon_2$ ) and depth of the second well ( $\epsilon_3$ ) for  $\mu_2 = 2.0$ .



Figure 3: Phase diagrams showing structures (top row) and coordination numbers (bottom row) of particles interacting via SG5 potentials with the gradual addition of second hump and third well. The height of the second hump ( $\varepsilon_4$ ) and the depth of the third well ( $\varepsilon_5$ ) are varied between 0 and 1. The state point with  $\varepsilon_4 = \varepsilon_5 = 0$  is the original two-well state point. The original structures from the two-well phase diagram are: (a,b) tI20-X ( $\varepsilon_2 = 0.0, \varepsilon_3 = 4.0, \mu_3 = 1.6$ ), with a third well located at  $\mu_5 = 2.5$ ; (c,d) cP4-Li ( $\varepsilon_2 = 2.0, \varepsilon_3 = 5.0, \mu_3 = 1.6$ ), with a third well located at  $\mu_5 = 2.5$ ; (g,h) cF4-Cu ( $\varepsilon_2 = 1.60, \varepsilon_3 = 2.00, \mu_3 = 1.78$ ), with a third well located at  $\mu_5 = 2.5$ .

self-assemble tP30-CrFe and cP8-Cr<sub>3</sub>Si when a third well is added, and the hP1-X (Figure 4c) state point self-assembles cI2-W. Figure 3g illustrates that the cF4-Cu two-well state point also self-assembles the cI2-W

structure.

If we start with the two-well tP30-CrFe state point, the structure switches to cI2-W with increasing  $\varepsilon_4$ . The switch to a higher coordinated structure occurs at a higher  $\varepsilon_4$  for the two-well tP30-CrFe than it does for the two-well tI20-X, cP4-Li, hP1-X, and cF4-Cu state points (Figure 3). This illustrates that tP30-CrFe is more stable than tI20-X, cP4-Li, hP1-X, or cF4-Cu in in the SG5 potential.

We next added a well to two state points of the LJG potential. These original structures were chosen because they are low-coordinated and we wished to determine if they would turn into higher-coordinated structures with the addition of a well. As with adding a well to SG3, we first varied the height of the added hump ( $\varepsilon_2$ ) and the depth of the added well ( $\varepsilon_3$ ) to observe how

gradually adding the hump and well changes the structure that forms. We observe that increasing the height of the added hump ( $\varepsilon_2$ ), increases the coordination number (Figure 5b, d). We then varied the the depth of the added well ( $\varepsilon_3$ ) and the location of the added well ( $\mu_3$ ) and observed that moving the added well to longer interparticle distances (increasing  $\mu_3$ ) increases the coordination number (Figure 5f, h). We believe that the structures tI10-X, tP32-X, and oC64-X are new structures not reported in the Inorganic Crystal Structure Database. Structural information is reported in Table 2.



Figure 4: Phase diagrams showing structures of particles interacting via SG5 potentials, upon varying the height of the second hump ( $\varepsilon_4$ ) and the location of the third well  $\mu_5$ . The original structures from the two-well phase diagram are: (a) tI20-X, (b) cP4-Li, (c) hP1-X, and (d) tP30-CrFe ( $\varepsilon_2 = 2.00, \varepsilon_3 = 2.66, \mu_3 = 1.70$ ).

Table 2: Crystallographic data for new crystal structures				
Pearson Symbol	Space Group	Unit Cell Parameters	Wyckoff sites	
tI10-X	I422	a: 2.4032 Å	$2b \ 0, \ 0, \ \frac{1}{2}$	
		c: 4.0032 Å	$8j x, x + \frac{1}{2}, \frac{1}{4}$	
tP32-X	P4/ncc	a: 2.9145 Å	$4c \ 0, \ \frac{1}{2}, \ z \ (z = 0.1771)$	
		b: 1.2481 Å	$4c \ 0, \ \frac{1}{2}, \ z \ (z = 0.4509)$	
			$8f x, x, \frac{1}{4} (x = 0.1646)$	
			16g x, y, z (x = 0.3454, y = 0.3095, z = 0.0824)	
oC64- $X$	Cmme	a: 3.8892 Å b: 3.9347 Å	160 x, y, z (x = 0.3281, y = 0.0898, z = 0.2167) 4b $\frac{1}{2}$ , 0, $\frac{1}{2}$	
		c: 4.1401 Å	$x_4^{4}, x_7^{2}, y_2^{2}$ 8n x, $\frac{1}{2}, 0.2858$ (x = 0.1719, z = 0.2858)	
			8m 0, y, z (y = 0.0898, z = 0.0756)	
			$8i \frac{1}{4}, x, 0 \ (y = 0.1414)$	
			$4f\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	
			$4q \stackrel{4}{0}, \frac{1}{4}, \frac{4}{2} (z = 0.8347)$	
			$8m \ 0, y, z \ (y = 0.0826, z = 0.3693)$	
			$4g \ 0, \frac{1}{4}, z \ (z = .5660)$	



Figure 5: Phase diagrams for particles interacting via LJG potentials with an added well. (a) Structures and (b) coordination numbers for adding a third well to a two-well cP1-Po state point ( $\varepsilon_1 = 1.3, \mu_1 = 2.0$ ), varying  $\varepsilon_2$  and  $\varepsilon_3$  between 0 and 1 for  $\mu_4 = 2.2$ . (c) Structures and (d) coordination numbers for adding a third well to a two-well hP1-Ca<sub>0.15</sub>Sn<sub>0.85</sub> state point ( $\varepsilon_1 = 1.27, \mu_1 = 4.6$ ), varying  $\varepsilon_2$  and  $\varepsilon_3$  between 0 and 1 for  $\mu_4 = 2.2$ . (e) Structures and (f) coordination numbers for adding a third well to the same cP1-Po state point, varying  $\varepsilon_3$  and  $\mu_3$ .



Figure 6: Unit cells for new structures (a) tI10-X, (b) tP32-X, (c) oC64-X.

#### IV Discussion

We observe that adding a third well to the SG3 interaction potential causes the original structure to turn into a higher-coordinated structure. One possible explanation for this is that, as the height of the second hump increases, particles are less able to move beyond that hump and are pushed together in the first two wells. However, this does not preclude the fact that there are state points with  $\varepsilon_4 = 0$  that form the highercoordinated structure (Figure 3e, g).

There is little diversity in the structures observed for the SG5 potential when the height of the second hump and the depth of the third well are significant, meaning  $\varepsilon_4$  and  $\varepsilon_5$  have values greater than 1 (Figure 4). In these parts of parameter space, we only see the most highly coordinated structures cP8-Cr<sub>3</sub>Si, tP30-CrFe, and cI2-W. More state points must be searched before this conclusion is definite, but what we observe here suggests that longer-range interactions have less of an effect on crystal structure than shorter-range ones. When we keep the first two wells and the first hump fixed, varying the second hump and third well, we only observe 1–2 different crystal structures.

By adding a hump and a well to the interaction potential, we are adding constraints on which distances particles can adopt with respect to each other, thus limiting the number of structures that form. To examine this more closely, we could fix the parameters controlling the second hump and third well, while varying the parameters of the first hump and first two wells. We could then compare the variety in structures observed in the SG3 and SG5 potential phase diagrams.

As with the SG5 potential, increasing the height of the added hump of the LJG3 potential corresponds with an increase in coordination number (Figure 5). We observe a larger variety of structures for the LJG3 potential than than the SG5 potential. SG5 and LJG3 have equally long-range interactions, but because SG5 has three wells and LJG3 has two, they are not necessarily comparable. In fact, the LJG3 phase spaces (Figure 5e, g) are more similar to the SG3 ones (Figure 2a, c). This could suggest that the number of wells is important, not only how long-range the interactions are.

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### ASPARTAME DIFFERENTIALLY INFLUENCES THE GUT MICROBIOME AND BONE TISSUE STRENGTH BASED ON TYPE OF DRINKING WATER

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### ABSTRACT

The composition of the gut microbiome is associated with bone tissue-level strength. The current project analyzed the effects of zero-calorie aspartame sweetener on the gut microbiome and bone tissue-level strength. Mice received either zero-calorie aspartame sweetener in reverse osmosis drinking water or untreated reverse osmosis drinking water from 4 weeks to 16 weeks of age. At the time of euthanasia, the femora were collected, and the right femur underwent micro-computed tomography and mechanical testing. The collected data did not support the original hypothesis that zero-calorie aspartame sweetener affects the gut microbiome and bone tissue strength, as the previous study had concluded. However, the gut microbiome is highly volatile to different conditions and many factors, such as the type of drinking water, could have affected the results.

### I. INTRODUCTION

The gut microbiome is composed of trillions of microorganisms that work to support the overall health of the host. New research has shown several functional interactions between the gut microbiota and the individual. If the gut microbiome is altered, these microbes can affect the host's immune system, metabolic functions, and overall health. Gut microbiome research continues to make headway in understanding the microbiome's function in immunology and pathogenic diseases.<sup>1</sup>

Recent microbiome research has shown new associations between the gut microbiome composition and bone tissue properties. Earlier research in the field found that mice with alterations to their gut microbiome composition had changes in bone tissue-level strength relative to unaltered microbiome controls.<sup>2</sup> In a previous study by the Hernandez laboratory, seven different gut microbial populations were induced in mice, and the effects on bone tissue quality were observed.

Of the seven groups, two groups were of particular interest. One group was treated with neomycin in acidified drinking water from 4 to 16 weeks of age. After femur bone analysis, the neomycin-treated group showed a reduction in bone tissue-level strength.<sup>2</sup> It is imperative to recognize that

neomycin, an antibiotic active against gramnegative bacteria, knocks out several microbial species in the gut microbiome leading to downstream effects on bone tissue strength. The other notable group had a gut microbiome altered by the consumption of acidified drinking water with zero-calorie aspartame sweetener. The sweetener was initially used to counteract the bitter taste from the cocktail of antibiotics but unexpectedly enhanced bone tissue strength. At the conclusion of this study, it was unknown if the gut microbiome induced by the aspartame was the direct cause of the bone tissue quality alterations.<sup>2</sup>

Due to the previous study, the next step was to carry out follow-up studies to confirm the findings and understand the mechanism that led to the enhanced bone tissue strength. When the study was replicated with the aspartame in a different type of drinking water (reverse osmosis rather than acidified), the enhanced bone strength phenotype was not present. As a result, a second follow-up study was performed in reverse osmosis water to evaluate if the effect of aspartame on the gut microbiome and bone was dependent on the batch of mice used and the type of drinking water. The long-term goal of the current research is to identify the gut microbes contributing to the changes in bone tissue strength.

### **II. MATERIALS AND METHODS**

### Study Design

Animal procedures were approved by the local Institutional Animal Care and Use Committee. C57BL/6J mice were acquired (Jackson Laboratory, Bar Harbor, ME, USA) and bred via homozygous mating in a conventional animal facility. Breeder animals were housed in plastic cages filled with 1/4inch corn cob bedding (The Andersons' Lab Bedding, Maumee, OH, USA), given standard laboratory chow (Teklad LM-485 Mouse/Rat Sterilizable Diet) and water ad libitum, and provided a cardboard refuge environmental enrichment hut (Ketchum Manufacturing, Brockville, Canada).<sup>2</sup> At 4 weeks of age following weaning, male (n = 16) and female mice (n = 16) were divided into two groups (n = 8/group/sex). Animals were housed in cages consisting of 4 mice. Distinct gut microbiota were induced in one male and one female group with zerocalorie sweetener (n = 8/group, 10 g/L) in reverse osmosis drinking water and male and female untreated control groups (n = 8/group). The zerocalorie sweetener consisted of aspartame, dextrose with maltodextrin, and acesulfame potassium (Equal, Merisant Company, Chicago, IL, USA; 10 g/L). Fresh drinking water was given every 2 to 3 days. Continual treatment throughout growth simulates the effect of microbiome alterations on the development of the bone phenotype at skeletal maturity.<sup>2</sup> At 16 weeks of age, blood serum was collected prior to euthanasia. Immediately after euthanasia, the perigonadal fat pad, cecal contents, femora, and tibias were collected.

### Micro-computed tomography

The right femora were harvested, wrapped in phosphate buffered saline-soaked gauze, and stored in an airtight container at  $-80^{\circ}$ C. Images of the femoral diaphyseal cross section were obtained by micro-computed X-ray tomography (MicroCT) with a voxel size of 5 microns. A Gaussian filter was used to remove noise. A global threshold was used to segment mineralized tissue from surrounding nonmineralized tissue. The total area, cortical cross-sectional area, moment of inertia (I), distance from the neutral axis to the edge of the bone surface (c), and section modulus (I/c) were determined.<sup>2</sup> Section modulus is a calculation to relate torque to maximum stress within a cross-section. It is a good indicator of whole bone strength and considers the geometry of

the bone.<sup>3</sup> All calculations were done through ImageJ. Figure 1 shows a cross-section image of the mid-diaphysis of the right femur. This figure can be used to calculate the distance between the center to the edge of the bone (c) which is later used to calculate section modulus.



Figure 1. Cross-section image of the diaphysis of the right femur

### Mechanical testing

The right femora were thawed to room temperature in phosphate buffered saline and tested in the anterior-to-posterior direction to failure in threepoint bending at a rate of 0.1 mm/s using a span length of 7.5 mm between outer loading pins (858 Mini Bionix; MTS, Eden Prairie, MN, USA). Force and displacement measurements were collected using a 25 lb load cell (SSM-25 Transducer Techniques, Temecula, CA, USA) and a linear variable differential transducer at a 100-Hz sampling rate.<sup>2</sup>

Three-point bending provides information about the structure of the whole bone, such as strength and stiffness.<sup>4</sup> Peak bending moment was calculated. The relationship between whole bone strength and section modulus was examined to indicate changes in bone tissue strength.



Figure 2. Schematic image (not to scale) of the three-point bending on the right femur bone

### **III. RESULTS AND DISCUSSION**

### Bone geometry

Treatment with zero-calorie aspartame sweetener causes no change to the cross-sectional area. In Table 1, male mice that received zero-calorie aspartame sweetener did not have any observable differences in cross-sectional area (p = 0.050). In Table 2, there was no significant difference between the untreated and treated female groups for the crosssectional area (p = 0.169). From the c-value and moment of inertia, section modulus was calculated. There was no statistical significance in section modulus between the two male groups (p = 0.102) and between the two female groups (p = 0.101).

Table 1. MicroCT results and calculations for untreated and treated groups of male mice

	CSA (mm <sup>2</sup> )	Section modulus (mm <sup>3</sup> )	
Untreated1.054Aspartame1.114		0.592	
		0.551	

Table 2. MicroCT results and calculations for untreated and treated groups of female mice

	CSA (mm <sup>2</sup> )	Section modulus (mm <sup>3</sup> )
Untreated	0.807	0.183
Aspartame	0.787	0.171

### Bone Tissue Strength Analysis

Maximum moment and bone tissue strength were calculated from three-point bending. In Figure 3, the maximum moment from mechanical testing, also known as whole bone strength, is related to section modulus from MicroCT. There is no statistical significance between the bone tissue-level strength of the zero-calorie aspartame sweetener and untreated male groups (p = 0.407). Comparatively, there is no statistical significance between the bone tissue-level strength of the treated and untreated female groups (p = 0.371). The linear regression lines indicate no difference between treated and untreated and untreated groups.

Therefore, we found that bone tissue strength was not increased when the zero-calorie aspartame sweetener was administered in reverse osmosis water rather than acidified. We attribute any prior observations that the zero-calorie aspartame sweetener had on bone tissue strength being related to the type of water the aspartame sweetener was dissolved in (acidified versus reverse osmosis).



Figure 3. Plot of Whole Bone Strength versus Section Modulus

A pH test was conducted to compare water samples from each study to understand why the results varied between the original study and the current study. The original study used acidified drinking water because, at the time of the study, the animal facility used this method to sterilize their drinking water. Since that study, the facility changed its sterilization protocols and switched to reverse osmosis drinking water. In Table 3, experiment results concluded that acidified water is about 10<sup>4</sup> times more acidic than reverse osmosis drinking water. It is likely that this could affect the gut microbiota that can thrive in the large intestine: encouraging the growth of some and diminishing the growth of others. However, further testing is required to confirm this hypothesis. Overall, water could be a potential factor that affects the gut microbiome and could be a reason for varying results among the studies.

Table 3. Results of the pH test of acidified and reverse osmosis drinking water

	Acidified	Reverse Osmosis	
Untreated	2.69	6.65	
Aspartame	2.74	6.43	

### **IV. CONCLUSION**

Zero-calorie aspartame sweetener in reverse osmosis drinking water does not affect the gut microbiome in a way that alters bone tissue strength. This study is important for future gut microbiome research and could help explain why there is difficulty repeating microbiome studies. The gut microbiome is highly volatile and can change with even slight variations in conditions. Specifically, between the original study and the current project, acidified water versus reverse osmosis drinking water could significantly affect the interaction of zero-calorie aspartame sweetener with the gut microbiota.

In the future, it is imperative to report any chance of variability among studies, including the type of water used, where and how the mice are bred, environmental changes, geographic location, and any other factors that could potentially affect the bacteria in the gut. Future gut microbiome work should focus on reproducibility and aim to keep the experimental environment as controlled as possible.

### V. ACKNOWLEDGMENTS

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### In-situ Investigation of Printing Immiscible Alloys Using Laser Powder Bed Fusion

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Additive manufacturing has tremendous potential for novel materials and manufacturing processes. In addition to fabricating parts with unique geometries and structures, it is also being studied with reference to new materials. For example, in this study, laser powder bed fusion (LPBF) was investigated for the potential printing of entirely new materials due to the rapid solidification of the melt pool. One such new material, investigated in this paper, is an aluminum-tin alloy with potential applications as a bearing material. This Al-Sn alloy was previously impossible to produce due to the large miscibility gap. However, by rapidly heating the metal powder with a high-powered laser and cooling the melt pool at an extremely fast rate, LPBF may soon enable the production of parts with previously unseen homogeneous immiscible alloys. This paper aims to develop a framework to study the manufacturing of immiscible alloy systems using in-situ radiograph images taken by a high-energy synchrotron source.

### I. Introduction

Additive manufacturing (AM) is seen as one of the next frontiers in fabrication of industrial and consumer products because of several unique characteristics. One such characteristic is the ability to create materials that were previously impractical to produce, such as immiscible metals that will separate out into their constituent phases when mixed by conventional methods. Instead of forming a homogeneous mixture, they phase-separate out due to their miscibility gap. An example of this can be seen below in Figure 1.



Figure 1: Binary Phase Diagram of Al-Sn [1]

This miscibility gap in the Al-Sn material system is due to the large differences in density, liquidus temperature, and surface tension, in addition to the varying crystal structures formed. To overcome this miscibility gap and form alloys of immiscible metals, there are two commonly researched approaches: mechanical alloying and rapid solidification.

Mechanical alloying is a solid-state powder processing technique in which metal powders are repeatedly sintered using a hot isostatic pressure (HIP) process similar to that of ceramic sintering. While it is a foundational process for synthesizing advanced materials, it can be challenging due to porosity, powder contamination, and inhomogeneities in the final product [2].

In contrast, this project focused on using rapid solidification of metal powders. This was done using laser powder bed fusion (LPBF)—an additive manufacturing technique in which a high powered laser selectively melts metal powder on a substrate to produce mechanical parts. In this way, the laser can melt and solidify the metal powder in fractions of a second—producing a cooling rate significantly faster than by conventional methods. An image of a similar setup to that of this project can be seen below in Figure 2.



By cooling the material at a faster rate, a more homogeneous microstructure can be produced because nucleation of different phases and diffusion of different atoms is limited. The goal of this project is to study this phenomena using in-situ imaging of LPBF to develop a framework connecting initial print parameters to final print characteristics.

### II. Methods

The trials for this project were conducted at the Advanced Photon Source at Argonne National Laboratory, a high-energy synchrotron source funded by the US Department of Energy.

For this project, specifically, the material system was a 50-50 ratio (by mass) of aluminum and tin powders on an aluminum substrate in an argon-rich environment. Under these conditions, print trials were conducted with laser power varying from 300 Watts to 375 Watts and scanning velocity ranging from 500 m/s to 600 m/s. During the single-layer line scans (as well as spot-welded samples), the high-energy x-rays were used to take radiograph images of the prints in-situ. These images were recorded using a high-speed

camera that allowed for a very high frame rate to observe phenomena within the melt pool.

These videos were then analyzed using ImageJ after being run through filters that magnified or reduced image components for clarity of different phenomena. Initially, a cursory analysis of the synchrotron videos and a comparison of the spot-weld and line-scan samples was conducted to understand the solidification processes. These can be found in Figure 4. To measure these values, the distance traveled by the solidification front was divided by time elapsed.

Next, an analysis of the solidification fronts of the line-scan videos was conducted to find correlation between the velocity of the solidification front and the scanning speed and laser power parameters. The purpose of these graphs (which can be found below in Figure 5) was to find any correlations between the laser conditions and the solidification speed.

After an investigation into various dimensionless numbers for fluid mechanics, the Weber Number and Péclet Number were chosen as quantities that could compare the phenomena within the melt pools and potentially lead to correlation with the homogeneity of the melt pool. The Weber Number is calculated using the formula:

We = 
$$\frac{\rho V^2 L}{\sigma}$$

The Weber number is essentially a comparison between inertial forces and surface tensional forces and a high Weber number indicates that the inertial forces are dominant. The Péclet Number is calculated using the formula:

$$Pe = \frac{VL}{\alpha}$$

The Péclet Number can be thought of as a ratio of convection to conduction within the melt pool. A large Péclet Number indicates convection is dominant within the melt pool. The variables for these formulas can be observed below in Table 1.

Variable	Description
V	Characteristic Flow Velocity (m/s)
L	Characteristic Length (m)
ρ	Density (kg/m <sup>3</sup> )
σ	Surface Tension (N/m)
α	Thermal Diffusivity (m <sup>2</sup> /s)

	Table 1	: Variables in	n Weber and	<b>Péclet Numbers</b>
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The Weber Number (and to some extent the Péclet Numbers) were then compared with homogeneity data to investigate correlation between those two values. This will be explained further in the results section.

To quantify the degree of homogeneity, two approaches were taken. Using grayscale profiles of SEM images, plots were created (much like the plot in Figure 3) of grayscale values with respect to distance across the line. These profiles were created from 250-pixel lines in ImageJ, taken horizontally every 60 pixels down throughout 125 micron scans.

To analyze the homogeneity of the prints, the first approach was to calculate the average standard deviation of the grayscale values. The purpose behind this method was that it would identify the presence of outliers and quantify the homogeneity of the data itself. This can be observed below in Figure 6 with respect to P/V ratio and Weber Number. While this method does identify outliers, it does not directly indicate homogeneity because it does not take the position of these outliers into account (well-dispersed outliers would indicate high standard deviation but would still be largely homogeneous).



Grayscale Values Across SEM Image



**Figure 3: SEM Image and Subsequent Profile** 

The second approach to quantify homogeneity was to count the number of peaks in the grayscale plots. This is because the scans taken across a constant distance will prove more homogeneous if there is a greater concentration of mixed aluminum and tin sections, and, therefore, more peaks in the grayscale values. This also means that the print is less homogeneous if there are fewer peaks due to the presence of Al-rich or Sn-rich sections. This data is plotted with respect to P/V ratio and Weber number below in Figure 7.

### III. Results

After analyzing the solidification front of both a spot-welded Al-Sn control sample and a line-scan printed sample, it was clear that the line-scan was solidifying at a much faster rate (in fact, 89% faster)—likely due to the horizontal nature of the solidification front rather than the radial solidification front in the spot-welded sample. This can be seen below in Figure 4. This result was evidence of the initial hypothesis that a moving laser in a line scan using LPBF would change the solidification process and allow for different microstructures to form.



Figure 4: Solidification front velocity of line-scan and spot-welded samples

Next, two clear trends were observed when comparing the solidification front velocity and print parameters (in Figure 5). First, it is clear that increasing the scanning speed of the laser is correlated to a faster solidification front velocity. This confirms the previous hypothesis that moving the laser across the powder layer at a higher speed would be correlated to the speed at which the melt pool solidified.

Second, the data shows that, generally, increasing the laser power leads to a slower solidification front. This also makes logical sense because heating the powder to a higher temperature means it will take longer to cool and solidify.

However, it is important to note that these graphs do not tell the entire story because they do not account for keyholing, balling, or lack-of-fusion defects that can form outside of the conduction region. This is simply a starting point that suggests more trials should be done and indicates a trend that should be considered along with other prior data on various print parameters.





Comparing Solidification Speed to Laser Power



Figure 5: Solidification Front Velocity as a Function of Scanning Speed and Laser Power

Next, comparing the Weber Number and standard deviation of grayscale values in the subsequent prints indicates that the initial hypothesis was correct: a higher Weber Number may lead to increased homogeneity. A larger Weber Number, which is indicative of higher turbulence within the melt pool, was considered in this section because it incorporates both melt pool velocity and material parameters into a value that can be compared across material systems. More data and repeated trials are necessary to form an actionable conclusion but Figure 6 shows a significant correlation between the turbulence of the melt pool and relative homogeneity of the final print.



Figure 6: Weber Number and Average Grayscale Standard Deviation compared to Ratio of Laser Power to Scanning Velocity

Based on the second method of quantifying homogeneity, Figure 7 shows that there is similarly a correlation between the Weber Number and the average number of peaks in the grayscale plots. Unlike in Figure 6 where a greater homogeneity was represented by a lower value (a lower standard deviation) the graph in Figure 7 shows the same rough correlation in which the more homogeneous the sample was, the more peaks it had and the larger the Weber Number (with some outliers).

Much like the data in Figure 5, more work will need to be done to come to an actionable conclusion linking the Weber Number to the homogeneity of the final prints. However, there does seem to be a correlation that makes logical sense based on the concept that increasing the turbulence and fluid velocity of the melt pool will lead to a better mixed and more homogeneous final print (assuming the parameters remain within the conduction zone and the print does not have noticeable microstructural defects).





Figure 7: Weber Number and Number of Peaks compared to Ratio of Laser Power to Scanning Velocity

### IV. Conclusions

The most important takeaway from this project was the correlation found between the Weber Number of the various print processes and the homogeneity of the final printed line scans. Without data from EDX analysis, it is still unclear exactly which method for measuring degree of homogeneity is more fitting but with more prints and a larger range of data, it will be possible to conduct similar analysis to additional experiments. More trials will need to be conducted on this experiment (likely including a wider range of printing parameters and thermal imaging data from the synchrotron source) but this data does suggest a trend that should be considered for future prints.

This framework comparing the Weber Number and homogeneity can also be applied to different print parameters (assuming they are inside the conduction zone) as well as other material systems to gain a better understanding of the phenomena occurring within the melt pool while printing metal powders using LPBF.

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### **Characterization of Powdered Makeup Using Several Techniques**

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### Abstract

This paper provides a characterization of four samples of powdered makeup (powdered eyeshadow from L'Oréal, Harvest, and Is'Mine, and a sample of face powder from Physician's Formula) with special attention paid to potential health concerns. Health risks examined in this characterization were common metallic allergens (specifically chromium, cobalt, and nickel) and potentially respirable metal oxide nanoparticles. To accomplish this, SEM imaging, TEM imaging, EDS, XPS, and XRD techniques were used. Results showed that chromium, cobalt, and nickel were not detectable in any of the samples and that the majority of the particles in all samples were larger than what is considered to be nanometer scale. The implications of these results on consumer safety are positive, as it is unlikely that the products tested in this work would pose a health risk due to the investigated factors to the average consumer using the products as directed.

### Introduction

Powdered makeup is a common, daily-use product worn by many across the world. In this project, four samples of powdered makeup were examined by several techniques to characterize them, especially with regard to possible health risks. Chromium, cobalt, and nickel are considered to be skin sensitizers and are common metallic allergens, so these were elements of interest when determining composition.<sup>1,2</sup> The International Organization for Standardization defines "nanoparticle" as having all dimensions in the nanoscale (approximately 1 nm to 100 nm),<sup>3</sup> though that definition has not necessarily been globally adopted at this time - for example, the US Food and Drug Administration (USFDA) defines nanoparticles as having at least one dimension in the nanoscale.<sup>4</sup> Likewise, potential health risks associated with nanoparticle exposure are not fully understood or agreed upon;<sup>5</sup> however, there is some concern over inhalation risks. Due to their small size, inhaled nanoparticles penetrate deep into the lungs to the alveolar region (see Figure 1), where they can deposit. The alveolar region has been found to be the primary area of deposition for particles smaller than 2  $\mu$ m in diameter, with no detectable deposition higher in the respiratory path.<sup>6</sup> There has been some evidence of inflammation of the lungs in rats and mice when repeatedly exposed to airborne titanium dioxide nanoparticles.<sup>7</sup> Oxidative stress and the resulting damage has been of concern as well for some nanoparticle compositions. This is not strictly limited to damage within the lungs, as inhaled nanoparticles are able to enter the bloodstream and therefore gain mobility to other areas of the body.<sup>5</sup> Uncoated zinc oxide (ZnO) and titanium dioxide (TiO<sub>2</sub>) nanoparticles have been associated with a risk of oxidative stress in both in vivo and in vitro studies. Oxidative stress, or a buildup of reactive oxygen species (ROS), can lead to genotoxicity, or damage to genetic material — though it should be noted that ROS do not always cause damage to DNA, and oxidative stress is not the only mechanism to cause genotoxicity.<sup>7-9</sup> Generally, current evidence suggests that dermal applications of these nanoparticles present little cause for concern, but there may be risks associated with respirable forms (though more, larger studies should be conducted for further investigation). As such, the Scientific Committee on Consumer Safety (SCCS) has approved TiO<sub>2</sub> nanoparticles for use in dermal applications when suspended in a

cream, such as in sunscreen, as absorption through the skin has not been found to be significant, but has recommended that  $TiO_2$  nanoparticles not be included in products that may be inhaled, such as powdered or sprayable products, due to insufficient data to confirm safety. However, "pigmentary titanium dioxide" (larger than 100 nm in diameter) has been approved for use in powders up to 25% and sprays up to 1.4% for general consumers.<sup>10–12</sup>

Samples included in this study were samples of powdered eyeshadow from L'Oréal, Harvest, and Is'Mine, and a sample of face powder from Physician's Formula. To determine elemental composition and therefore possible inclusion of skin sensitizers or common metallic allergens, compositional analysis was performed by EDS, XPS, and XRD. To determine potential inclusion of nanoparticles and to characterize particle shape and size, samples were examined by SEM and TEM microscopy.



Fig. 1: Diagram of the lungs, including alveoli<sup>13</sup>

### Procedure

### Scanning Electron Microscope

Each sample was first examined by scanning electron microscopy, using a Zeiss LEO 1550 FESEM and a Zeiss Gemini 500 SEM. Samples were prepared for SEM imaging by applying a small amount of powder to a circle of carbon tape on an aluminum puck. Excess powder was blown off of the tape with compressed air. The sample puck was then coated with carbon using an evaporation sputter coater, to prevent charging of the sample and ensure adhesion of the sample powder to the puck. For SEM imaging, an EHT (electron high tension), or accelerating voltage, of 3.00 kV and a working distance of around 5 mm (5.0-5.3 mm) were used with an SE2 (secondary electron) detector. An image using a backscatter detector was also taken of the L'Oréal sample, at an EHT of 7.00 kV and a working distance of 8.2 mm. EDS was performed alongside imaging with the SEM and was calibrated with copper and aluminum references before data collection. First, a large area scan (100  $\mu$ m across) of each sample was performed at an EHT of 30 kV and a working distance of around 7 mm (7.0–7.3 mm), in order to get an idea of the elements present and make a plan for the proper EHT for further scans. Based on these initial spectra, the following EHT values were chosen for further scans: 30.00 kV for the L'Oréal sample to account for the presence of bismuth, 15.00 kV for the Harvest sample to account for titanium, 18.00 kV for the Is'Mine sample to account for iron, and 20.00 kV for the Physicians Formula sample to account for zinc. Carbon coating was chosen for sample prep rather than a gold-palladium coating in order to not add additional extraneous signals to the EDS spectra.

### Transmission Electron Microscope

Samples were also examined by transmission electron microscopy using an FEI Tecnai 12 BioTwin TEM and an FEI F20 TEM STEM, and were prepared in two ways. First, in order to characterize the nanoparticle inclusions, the sample powder was added to IPA (isopropyl alcohol) in a small beaker, which was new and had been cleaned with a sonicator. All large clumps of powder were broken up with a spatula, then the IPA and powder mix was sonicated for 10 minutes. This solution was then allowed to settle for 10 minutes. After settling, a 200-hex mesh copper TEM grid with a lacy carbon coating was quickly dipped into the top of the supernatant and allowed to dry. This prep was completed for each of the four samples. These grids were then

imaged at an EHT of 120 kV and ImageJ software was used to determine the sizes of imaged particles. Diffraction patterns were collected for several particles to determine crystallinity of each particle. Second, in order to determine the potential crystallinity and elemental composition of larger particles, FIB (focused ion beam) techniques were used to mount and thin selected particles for TEM imaging (a Thermo Fisher Helios G4 UX FIB was used). This technique, using a germanium ion beam, was used on the L'Oréal and Physician's Formula samples: for L'Oréal, a broad, flat particle (approximately 10.2  $\mu$ m by 6.7  $\mu$ m) was chosen and for Physician's Formula a spherical particle (at least 3  $\mu$ m in diameter) was chosen. For both, the sample powder was initially prepared in the same manner as described in the SEM section. These sample pucks were loaded into the FIB and an appropriate particle was chosen using SEM techniques. The selected particle was then removed and attached to the copper grid with a platinum deposit. The desired area was then thinned with the ion beam so as to make the area electron transparent for TEM imaging. These thinned samples were then imaged at an EHT of 200 kV. EDS analysis was performed on both samples and diffraction was examined for the spherical particle.

### X-ray Photoelectron Spectroscopy

XPS was completed using a Fisons SSX-100 ESCA spectrometer. Sample prep for XPS was similar to that for SEM — carbon tape was placed onto a large, multi-sample puck, onto which the sample powder was applied. Excess powder was blown off, being careful not to blow powder onto adjacent tape and therefore contaminate other scans. This sample puck was not coated, as XPS is extremely surface sensitive and doing so would affect the data significantly. To account for potential charging, an electron flood gun was used. A survey scan (data collected over a long range of possible kinetic energy values of the photoelectrons) was conducted for each sample to get an overview of the elemental composition. Additionally, a high-resolution scan (data collected over a small range of possible electron kinetic energy values centered on a known energy for an element of interest) was collected for magnesium and carbon in the Harvest sample. The carbon 1s peak, which occurs at a known binding energy value of 285 eV, was used to calibrate the analysis software — referencing the spectra to the C1s peak to account for peak shifts caused by charging in the sample. The magnesium high-resolution scan was conducted with the Auger peak that occurs at a binding energy of 300–306 eV because magnesium's photoelectron peaks (Mg 2s and Mg 2p) were overlapping with other peaks and were therefore not clear.<sup>14</sup> A second survey of the Harvest sample was conducted after the high-resolution magnesium scan to check if any changes had occurred in the sample as a result of the scan. Analysis was conducted with CasaXPS software.

### *X-ray diffractometer*

The diffraction pattern for each sample was obtained with a Bruker D8 Advance ECO powder diffractometer. Each powder was packed into a well in a quartz sample holder. These samples were then loaded into the diffractometer and examined with x-rays from a copper source at 40 kV and 25 mA (see Figure 2). The incident x-rays were monochromated with nickel foil and the diffracted x-rays were detected with a 160-channel silicon strip detector. The resultant data was analyzed with MDI's JADE software.



Fig. 2: Sample set up in diffractometer

### **Results and Discussion**

### Dimensions of Particles

All four samples had the majority of their bulk in flaky particles, with many layers stacked together (see Figure 3 for representative SEM images). This stacking, or clumping together, was most evident in the Harvest sample, which had the least visual variation in the SEM images of the particles. The Harvest sample also had the smallest of the large, bulk particles: with an average representative particle size of approximately 9  $\mu$ m by 13  $\mu$ m. The other samples had more variation in the size of the larger bulk particles, each including some that were a few micrometers across to tens of micrometers (see Table 1 for comparisons of average sizes). The L'Oréal and Physicians Formula samples also included spherical particles sized in the micrometer scale, also ranging from a few micrometers to tens of micrometers in diameter, but with a typical size of about 11  $\mu$ m in diameter in both samples. As found by TEM imaging, all four samples included nanoparticles however, they were not the majority of the particles present, as determined by electron imaging and supported by the low width, or high "sharpness," of the XRD peaks for the relevant compound (specifically TiO<sub>2</sub>, as this was the most common nanoparticle across the samples). The following order of concentration of nanoparticles was determined by SEM imaging, listed from highest to lowest: Physicians Formula, L'Oréal, Is'Mine, Harvest. However, even for the Physicians Formula and L'Oréal samples, the majority of particles were on the micrometer scale.



*Figure 3: Representative SEM images of the L'Oréal (top left), Harvest (top right), Is 'Mine (bottom left), and Physicians Formula samples (bottom right)* 

Property	L'Oréal	Harvest	Is'Mine	Physicians Formula
Average size of flakey material	Approx. 15 $\mu$ m by 23 $\mu$ m (medium variability — average standard deviation 9 $\mu$ m)	Approx. 9 $\mu$ m by 13 $\mu$ m (low variability — average standard deviation 5 $\mu$ m)	Approx. 15 $\mu$ m by 22 $\mu$ m (highest variability — average standard deviation 10 $\mu$ m)	Approx. 12 $\mu$ m by 18 $\mu$ m (medium variability — average standard deviation 8 $\mu$ m)
Average size of spherical particles	Approx. 11 $\mu$ m diameter (standard deviation 5 $\mu$ m)	N/A	N/A	Approx. 11 $\mu$ m diameter (standard deviation 4 $\mu$ m)
Relative amount of nanoparticles	Second highest	Lowest	Second lowest	Highest

Table 1: Physical properties of powders as determined by electron microscopy for comparison

### Elemental Composition

According to the EDS spectra, the general compositions of the powders were fairly similar, with common elements being carbon, oxygen, silicon, magnesium, aluminum, potassium, iron, and titanium in different concentrations. XPS data supported this result, showing that for each powder the most abundant element by atomic percent was carbon, the next most abundant was oxygen, and the third most abundant was silicon — though the actual percentages varied, this order was consistent for all four samples. However, the samples showed variation in the elements of lower concentrations. L'Oréal included bismuth, chlorine, and calcium, Is'Mine included sodium, and Physician's Formula included sodium and zinc.

Spot spectra were collected in EDS on the nanoparticles in the L'Oréal and Physicians Formula samples and the bulk that the nanoparticles rested on, and were then compared to determine the composition of the nanoparticles. By this method, the nanoparticles in the L'Oréal sample were determined to be titanium dioxide, and the Physician's Formula sample was determined to contain nanoparticles of titanium dioxide, zinc oxide, and iron oxides. Elemental mapping was also conducted with EDS on the small particles using the transmission electron microscope for the Physician's Formula sample. This showed a titanium dioxide particle of 230 nm by 130 nm and an iron oxide nanoparticle of 75 nm by 100 nm, further supporting those compositions (see Figure 4).



Fig. 4: TEM image and titanium and iron EDS maps of Physicians Formula sample, showing titanium-based and iron-based small particles

A backscattered electron image was also collected for the L'Oréal sample (see Figure 5). Backscattered electrons are atomic-number dependent, so the higher the atomic number, the brighter it will appear in the image. The backscattered image showed several bright particles: by using EDS analysis on these regions, it was determined that all of the brightly lit regions in the backscattered image contained bismuth and chlorine, and, based on the spectra composition, that the most likely compound was bismuth oxychloride (BiOCl).

Both the L'Oréal and Physicians Formula samples contained micro-scale spherical particles, but they differed in composition. The spheres in the L'Oréal sample were carbon-based, while those from the Physician's Formula sample were silicon dioxide, as determined from EDS data (see Table 2 for the EDS data used to confirm SiO<sub>2</sub>). A silicon dioxide sphere was thinned and examined with TEM diffraction to determine the crystallinity. As it did not create a distinct diffraction pattern, instead forming broad rings as is typical for amorphous silica, it was determined that the spheres consisted of amorphous rather than crystalline silicon dioxide (see Figure 6). However, the XRD data for Physician's Formula did show diffraction patterns consistent with crystalline silica, so the sample also likely included crystalline silica in the flaky particles.



Fig 5: Backscattered electron image of the L'Oréal sample

Element	Atomic Percent
O K	66.32
Si K	33.53
Cl K	0.12
Ti K	0.01
Fe K	0.01





Fig 6: Electron diffraction from amorphous SiO<sub>2</sub> sphere

A high-resolution XPS scan was obtained for the magnesium Auger peak in the Harvest sample. This produced a single peak that was shifted to a slightly higher binding energy than typical for magnesium (centered at 307 eV), even after charge correction, which is consistent in shape and energy with magnesium in an oxide rather than the metal form.<sup>14</sup> After running a high-resolution scan, another survey of the sample was collected. This showed a lower atomic percent of magnesium, indicating that the sample was degrading (see Figure 7). This occurs with organic molecules, which seems to support the claim that the magnesium in the Harvest sample is derived from magnesium stearate, not talc. This conclusion was also supported by the lack of reasonable matches to the diffraction associated with talc in the XRD data.



Fig. 7: XPS survey scans before (left) and after (right) a high-resolution scan for the magnesium Auger peak (center) on the Harvest powder

### Conclusions

In this work, four samples of powdered makeup (eyeshadows from L'Oréal, Harvest, and Is'Mine and face powder from Physicians Formula) were characterized, with special attention paid to determining the presence of commonly allergenic metals and of metal oxide nanoparticles. Chromium, cobalt, and nickel — known to be common skin sensitizers and allergens<sup>1,2</sup> — were not detectable in any of the samples by EDS or XPS. Nanoparticles, which could pose some health risks if inhaled<sup>7-9</sup> — a possibility in sprayable or powdered cosmetics — were also investigated. While all four powders had some amount of nanoparticles present (most commonly titanium dioxide, though the Physicians Formula sample also included particles of zinc oxide and iron oxides), the majority of particle sizes were in the microscale (greater than 100 nm). Interestingly, at the time of writing this paper, Harvest claims on their website that their products do not contain nanoparticles.<sup>15</sup> While the Harvest sample had the fewest nanoparticles of the four brands tested, a small amount was found in TEM imaging. However, as the majority of the particles were sized in the microscale, it is unlikely that the nanoparticles present would pose a substantial health risk to the average consumer, using the product as advertised. Current SCCS opinions on titanium dioxide in cosmetics include guidelines that state "pigmentary titanium dioxide" (larger than 100 nm in diameter) is considered safe for use in powders up to 25% and sprays up to 1.4% for general consumers,<sup>12</sup> so the inclusion of microscale titanium dioxide in the four powders tested in this work was not considered hazardous.

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### **Chiroptical Metamaterials**

### **Impact of Solvent Vapor Annealing on the Chiroptical Properties of CdS Chiral Thin Films**

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### Abstract:

Chiroptical metamaterials based on semi-conducting and metal nanocrystals are enabling a broad range of technological prospects due to their quantum confined electronic structures and enhanced signal when fabricated into chiral hierarchical superstructures. While monodisperse (1.5 nm) magic size clusters (MSCs) have been realized to self-assemble into thin films with enhanced interaction with chiral light, the approach to evaporation driven assembly is limited by the transport kinetics at the tri-phase contact line. Here, we report the enhancement of light-matter interaction (g-factor) in MSC thin films through solvent vapor annealing (SVA). Characterization of the thin films before and after SVA treatment revealed enhanced g-factors and structural changes leading to new insights on the length scale of chirality emergence, and design principles for optimizing chiroptical materials out of equilibrium. The prospect of utilizing SVA to re-equilibrate thin films is common in the soft matter community and has the potential to be used as a non-invasive, inexpensive technique to achieve robust metamaterials for device applications.

### I. Introduction

Chirality is a phenomenon ubiquitous in nature that emerges at all length scales, spanning from galaxies to sub-atomic particle spin states. The field of nanotechnology has grown rapidly with interest in the chirality of nanoparticles and their impact on light-matter interaction. Further research is needed in the field of chiral nanostructures to maximize use in applications such as sensors, catalysis, and photonic devices<sup>1</sup>. The chiroptical properties of a chiral nanostructured architecture can be quantified by their interaction with circularly polarized light. Significantly, these optical properties can be programmed through controlled self-assembly due to various coupling interactions between neighboring particles and the ensemble of structural ordering. In the context of fabricating novel chiroptical metamaterials, bottom-up manufacturing has shown to be an advantageous method to manufacture NP assemblies at low cost and with strong light-matter interaction. It is known that a higher structural order will increase the exciton coupling of nanocluster building blocks and increase the anisotropic signal (g-factor). Exploring methods to further optimize chiral assemblies, by enhancing their g-factor, is attractive; specifically, post-processing methods such as solvent vapor annealing (SVA) have been shown to increase order in soft matter systems<sup>2</sup>. Solvent vapor annealing is a convenient approach to non-invasively restructure and anneal solid-state matter by simply subjecting a film to increased vapor pressure by a compatible solvent.

In this paper, we report the impact of solvent vapor annealing on the structure and optical properties of CdS "magic-size cluster" (MSC) thin films. We draw insights and propose new questions based on the structure-property effects of post-processing CdS MSC thin films through SVA. Specifically, we will discuss the experimental optimization procedure, where we analyzed the effect of CdS MSC thin films under varying SVA parameters, and then draw insights into how chiroptical properties of thin films of varying thicknesses are impacted by SVA. Through this investigation, we hope to better understand the emergence and enhancement of chirality from nanocluster building blocks. The characterization of these thin films through circular dichroism spectroscopy and microscopy techniques will give insight into the limitations of kinetically trapped supramolecular structures and will display the advantage of using a simple post-treatment process. The prospect of optimizing non-equilibrium chiroptical metamaterials via inexpensive and scalable processes introduces opportunities for commercial applications.

### **II. Methods and Materials**

### MSC solution preparation

We investigated the structure-property effect of SVA on self-assembled CdS thin films. The first step of the process is to synthesize monodisperse ( $\sim$ 1.5nm) CdS magic size clusters (MSCs)<sup>3</sup>. Next, the MSCs were dissolved in hexane (20 mg/mL) and stirred for 24 hours, or until the viscosity of the solution increased and the bulk MSCs have fully dissolved.

### Glass cleaning procedure

Before we fabricate the thin film, it is important to make sure that the film is prepped on a clean glass slide. Glass slides were cut into  $2.5 \text{ cm}^2$  substrates and placed in a beaker for multiple wash cycles. Acetone was filled into the beaker, enough to cover the slides completely, and the glass slides were sonicated for 5 minutes. After the sonication process is complete, the glass slides were dried with an air gun and placed back into the beaker. The beaker was filled with isopropyl alcohol, and the sonication bath and drying procedure were repeated. Next, glass slides were placed into a UV ozone cleaner for 5 mins to remove extraneous organic matter.

### Thin film fabrication

Once the glass slides are cleaned and an MSC solution is made, the thin films can be fabricated. A separation gap between parallel plates is created by using double-sided tape on the four corners of the bottom glass substrates (note: the parallel plates are not together until *after* the solution is drop-casted). Once the tape is positioned at the desired interplanar distance, the solution is drop-casted on the bottom substrate and another glass substrate is placed on top. Throughout the drying process, thin films self-assemble on the top and bottom substrates. Each sample was periodically evaluated during drying to make sure the triphase contact line evaporated uniformly and radially. Samples that evaporated uniformly and radially were then separated and characterized accordingly.

### Circular dichroism (CD) spectroscopy

The samples are then evaluated under CD spectroscopy to analyze the film's interaction with circularly polarized light. Concurrently, the CD, linear dichroism (LD), and absorption were monitored and recorded. CD spectra were recorded and the same site before and after SVA treatment with a 4 mm aperture.

### Laser scanning confocal microscopy (LSCM)

The microstructure of the thin films before and after SVA testing was analyzed with a Keyence Optical Profilometer. Before and after SVA treatment, structural changes were quantified using FFT to follow the structural order of the periodic band textures displayed in the films.

### Solvent Vapor Annealing

The SVA system consisted of an air-tight jar, a crystallization dish to hold the solution, and a metal fixture to separate the sample from the liquid phase of the solvent. To prepare the system, the hot plate is turned on to begin heating up the chamber. After sitting on the hot plate at the proper temperature for about 30 minutes, the solution is then put into the system and the sample is fastened in the system. The system is left to anneal for a specified amount of time, and then the sample is immediately removed once the time ends so that any remaining solution will evaporate off the sample. Once the sample is dry, all of the post-treatment data is collected for analysis.

### **III. Results & Discussion**



**Figure 1:** Thin film fabrication and post-fabrication processing. (A) Hele-Shaw cell setup. Evaporation of MSC solution between two parallel plates creates enantiomeric thin films on top and bottom substrates. (B) Length scales of self-assembly. The 1.5 nm CdS cluster forms a hexagonal mesophase that self-assembles into fibers, bundles of fibers (filaments), and undulated bands across the cm length film. (C) Schematic of SVA chamber and corresponding components.

The solution that assembles the thin films is a solution composed of MSCs and hexane. The MSCs, made of cadmium sulfide, are monodisperse and form a discotic mesophase. The solution was evaporated in a parallel plate geometry for controlled evaporation and separated by a spacer (~100-500  $\mu$ m) (Figure 1A). Interestingly, the films formed on the top and bottom glass substrates are chiral. Upon self-assembly, the MSC nanoclusters structure themselves in a hexagonal lattice which then creates filaments that exhibit a twisted formation (Figure 1B). A high-quality film is shown to have a circular order of evaporation and visual iridescence when the dried film is held up to a light source.

There is no consistent system in place for solvent vapor annealing<sup>2</sup>, so we had to design our own. The first system we made had many design flaws. The glass container that held the sample had significant vapor leakage. We immediately had to correct the system so we chose to use an air-tight jar. We chose the jar because it was big enough to encapsulate the whole system and prevent vapor leakage (**Figure 1C**). We chose to use SVA because it is a less invasive and more convenient post-treatment process. This is a common process that provides a low-temperature approach to anneal soft matter films. The post-treatment will allow for the thin film to swell and reach a state closer to equilibrium which we hypothesize will create a stronger dipole coupling and larger anisotropy (g-factor).

We used a CD spectrometer to measure the thin film's absorption and absorption of circularly polarized light. With CD and absorbance, we calculated the dimensionless anisotropy of the system, g-factor:

$$g = \frac{\theta[mdeg]}{3.3^{*}10^{4}*Abs} \tag{1}$$

We then quantified the structural change of the sample by using a laser scanning confocal microscope (LSCM). We used a fast Fourier transform (FFT) analysis to convert the laser images to the frequency domain, where we can measure the periodicity of the thin films and band texture quantitatively.

The parameters for preliminary SVA testing were (1) treatment time under SVA and (2) temperature of the system. We wanted to test these to see where within these individual variables we see a more prominent shift in g-factor and/or structure. Once the desired system parameters were determined, we ran samples of different thicknesses under the optimal SVA chamber.



**Figure 2:** Structure and optical properties before and after SVA for two temperatures. (A-C) Thin film treated for 4 hours with hexane solvent at 55°C. Before (A) and after (B) structure of the thin film. (C) G-factor before and after SVA testing. (D-F) Thin film treated for 4 hours with octane solvent at 100°C. Before (D) and after (E) structure of the thin film. (F) G-factor before and after SVA testing.

For the first set of samples, we varied the time each sample spent in the chamber. Each sample for the time trial was maintained at 55°C with a hexane solvent. The first sample (S1 in Table 1) was run under the first system we created that had noticeable vapor leakage for 2 hours. We did not see any significant change in the g-factor after 2 hours but it was shown to increase by 0.9%. However, the samples run for 4 hours and 6 hours were shown to have a much more significant g-factor increase and structural change where there was minimal to no vapor leakage. The results of the g-factor shift and structure change between the 4 and 6 hours exceed 38%. That tells us that, in terms of a time variable, the optimal system should be run anytime between 4-6 hours.

Furthermore, we investigated the impact of increased temperature during SVA. In order to increase the temperature of the system without exceeding the boiling point of a solvent, we switched the solvent from hexane to octane. **Figure 2** shows the samples that were tested under the two temperature conditions. One sample was tested at 55°C with hexane as a solvent and the other was tested at 100°C with octane. The sample tested under the hexane solvent shows an increase in the order of the film however based on the optical data we see at 100°C, the sample became amorphous and much of the definition of the structure was lost. In terms of the g-factor shift, the sample at 55°C shows an increase of about 36%, but at 100°C, there was an inversion in chirality and the micro-structure appeared to have been altered. We do not understand the reason for the inversion and sign change in the g-factor yet. A summary of the preliminary testing conditions and g-factor results is reported in **Table 1**.

Sample ID	Solvent	Time SVA (hr)	Condition	G-factor Max	Percent change (anisotropy)
01	Harmer	2	Pre SVA	-0.0221	0.0
51	Hexane	2	Post SVA	-0.0223	0.9
60	Thomas	4	Pre SVA	0.0017	<b>CD 7</b>
52	Hexane	4	Post SVA	0.0027	0Z. /
02	LImmon	ć	Pre SVA	-0.0013	20 5
22	Hexane	6	Post SVA	-0.0018	28.2
<b>C1</b>	Octano	л	Pre SVA	-0.0017	63.5
51	[ Octane		Post SVA	-0.0028	
00	Octano	4	Pre SVA	0.0027	112.2
52	2 Octane	Octane 4	Post SVA	-0.0147	442.2
00	Octobe	4	Pre SVA	-0.0047	51.0
\$3	53 Octane	4	Post SVA	0.0021	-54.9

Table 1: Preliminary testing of SVA treatment on MSC thin films. Samples tes	ted under
hexane and octane were treated at 55°C and 100°C, respectively.	

After preliminary testing, we were able to deduct that the optimal system for testing going forward will be done between 4-6 hours and at 55°C. Under these parameters, we began to analyze the effect of SVA on samples of varying thicknesses. As previously mentioned, we created a gap for the parallel plates using pieces of tape. In order to increase the thickness of the film, we increased the spacing of the cell, which in turn would increase the thickness of the overall film. We tested 3 different thickness variables, with a constant solution volume of  $35\mu$ L, by varying the interplanar distance of the parallel plates to 100um, 300um, and 500um. Based on

the absorption graphs we see that we were able to successfully control the thickness of the sample (**Figure 3**). We verified that all samples exhibited a similar trend in microstructure variance. For each film, we observed the periodicity of the film decreases as we move further away from the center of the film,  $r/R_0=1$  where  $R_0$  is the radius of the film.



**Figure 3**: Characterization of thickness and thin film structure for films fabricated with 100 (blue), 300 (red), and 500 (black)  $\mu$ m interplanar distance. (A) Absorption of the thin films and (B) structural periodicity of the thin films where R<sub>0</sub> is the radius of each respective film.

Importantly, when we measured the chiroptical data of these films, we scanned the samples four times, including two measurements of the film facing toward and away from the light beam. We performed this procedure to ensure that CD and g-factor measurements were free of instrumental artifacts, and so we could identify linear dichroism-linear birefringence (LDLB) contributions<sup>4</sup>. We isolated the "true" CD and LDLB contribution with the following equations:

$$CD_{iso} = 0.5 \times (ECD_{Front} + ECD_{Back})$$
(2)  
$$LDLB = 0.5 \times \left(ECD_{Front} - ECD_{Back}\right)$$
(3)

Our findings for post-treating MSC thin films of various thickness are presented in **Figure 4**, and a summary of the chiroptical properties is presented in **Table 2**. The data shown in figure 4 show that after post-treatment, the g-factor and the CD of each sample increased, with no inversion of chirality. For the 100  $\mu$ m spacer sample, the g-factor increased by 38.5%, with the absolute value of the integral LDLB to CD ratio increasing from 2.03 to 2.35. For the 300  $\mu$ m spacer sample, the g-factor increased by 20.2%, with the absolute value of the integral LDLB to CD ratio increasing from 0.90 to 0.92. For the 500  $\mu$ m spacer sample, the g-factor increased by nearly 400%, with the absolute value of the integral LDLB to CD ratio decreasing from 1.99 to 0.48. Interestingly, based on FFT measurements, the 500  $\mu$ m sample shows a structural periodicity change from 3.35 to 3.77  $\mu$ m.

Our results show that using SVA for 4 hours at 55°C as a post-treatment method for MSC thin films increased the g-factor for each film of various thicknesses. Insights into the dramatic change in g-factor for the 500  $\mu$ m spaced sample are still being interpreted. However, we can infer from these samples that SVA is softening the thin films, changing the structural ordering, and further enhancing the dipole coupling of neighboring MSC clusters.



**Figure 4:** Structure and optical properties before and after SVA. (A-D) results from 100  $\mu$ m sample. (A) CD and LDLB contributions before and after SVA. (B) G-factor change before and after SVA. (C) Structure changes before, and (D) structure changes after SVA. (E-F) results from 300  $\mu$ m sample. (E) CD and LDLB contributions before and after SVA. (F) G-factor change before and after SVA. (G) Structure changes before, and (H) structure changes after SVA. (I-L) results from 500  $\mu$ m sample. (I) CD and LDLB contributions before and after SVA. (J) G-factor change before and after SVA. (K) Structure changes before, and (L) structure changes after SVA.

Sample ID	Condition	∫  CD <sub>iso</sub>	∬LDLB	ſ LDLB / ſ CD <sub>iso</sub>	Percent change (anisotropy)	
100 µm	Pre SVA	1431	2903	2.03	38.5	
	Post SVA	1663	3908	2.35		
300 µm	Pre SVA	6076	5487	0.90	20.2	
	Post SVA	1411	1300	0.92	20.2	
500 µm	Pre SVA	1695	3370	1.99	208.8	
	Post SVA	4427	2134	0.48	398.8	

 Table 2: Summary of chiroptical properties before and after SVA testing of MSC thin films of various thicknesses.

### **IV. Conclusion**

Overall, from our investigation of post-treating MSC thin films with SVA, we can make a few conclusions based on the data. Qualitatively, we observed a change in the structure for each of the samples we tested depending on the testing parameters of SVA. Quantitatively, we measured an increase in anisotropy for each thin film tested with hexane at 55°C. This leads us to hypothesize that the dipole coupling, and therefore structural arrangement, is improved at the intra-filament length scale. When fabricating the thin films, the structure is kinetically trapped when deposited onto the glass substrate. It is possible that after we perform SVA on the thin films, the structure is allowed to soften and reach a state closer to equilibrium after removing the thin film from the solvent environment. A future investigation will involve how the time allotted for drying, after SVA, impacts the kinetics. Specifically, in our experiments, we immediately removed the thin film from the hot plate, whereas a gradual decrease to room temperature may allow more time to reach an equilibrium state and produce larger g-factors.

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### Rational Design of High-Density Polyethylene with Targeted Physical Properties via Statistical Modeling of Molecular Weight Distributions

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Statistical measures of a molecular weight distribution (MWD), such as  $M_n$  (number average molecular weight) and D (dispersity), are frequently used to estimate the properties of polymers. However, common statistical metrics are insufficient for representing more complex (bimodal or trimodal) MWDs. This work expands upon previous models by incorporating an integration-based statistical method that maps the entire MWD of high-density polyethylene (HDPE) to its properties. The use of B-splines facilitated the creation of functions that could be be optimized via generalized Tikhonov regularization to predict various properties of HDPE. Our model was found to outperform a previous method that predicts physical properties using the statistical moments of a MWD.

### I. INTRODUCTION

High-density polyethylene (HDPE) is a commonly utilized polymer (plastic) in a multitude of industries due to its favorable toughness, processability, and price.<sup>1,2</sup> For instance, HDPE can be found as a component of bottles, food packaging, and natural gas pipes.<sup>2,3</sup> Recently, efforts to optimize and control the properties of polymers have focused on manipulating their molecular weight distributions (MWDs).<sup>4–7</sup> Since a polymer's weight is proportional to its length, the MWD can provide insight into the structure and physical properties of a material.

One example demonstrating this connection is apparent in a theory proposed by Huang and Brown,<sup>8,9</sup> which argues that high molecular weight components in HDPE MWDs are more likely to contain tie molecules. These molecules are long chains that connect adjacent crystalline regions in a polymer.<sup>8,9</sup> A standard test of a material's durability involves exerting a tensile force, and then recording the stress and strain required for it to break. In this context, a higher proportion of heavy molecular weights yields a stronger polymer, since there will be more tie molecules available to distribute the force.

As shown in Figure 1, a MWD can be represented using statistical measures such as the number average molecular weight  $(M_n)$  and dispersity (D). These metrics are often used to predict the properties of polymers, instead of incorporating the entire distribution.<sup>5,10,11</sup> Intuitively, a HDPE sample with a higher  $M_n$  is expected to be tougher, and possess a larger viscosity.<sup>12</sup> This indicates that there is an inherent trade off between the durability and processability of HDPE. However, there is a wide variety of MWDs that possess the same  $M_n$  and  $D^4$  Using the entire MWD as an input may reveal relationships between the structure of HDPE and its properties that traditional statistical measures fail to capture. Ideally, this would open the possibility for producing HDPE with previously unattainable combinations of processability and strength.

This research expanded upon these ideas by utilizing an integration-based statistical model to determine the



FIG. 1. A visual representation of a MWD, along with the corresponding  $M_n$  (depicted by the vertical line) and D (depicted by the arrows).

relationships that exist between the MWDs of HDPE, and an array of rheological and mechanical properties. The complex viscosities at shear rates of 2.5 radians/s (henceforth referred to as low shear viscosity) and 251 radians/s (high shear viscosity) encompassed the studied rheological properties. The studied mechanical properties included the stress at break, strain at break, toughness, and Young's modulus. The use of piecewise functions known as B-splines<sup>13</sup> and P-splines<sup>14</sup> facilitated the development of flexible functions that map an entire MWD to a corresponding set of properties, and adhere to smoothness restrictions imposed by generalized Tikhonov regularization.<sup>15</sup>

#### **II. COMPUTATIONAL METHODS**

For this work, Jenny Hu, under the supervision of Professors Brett P. Fors and Geoffrey W. Coates, created the MWDs of 100 samples of HPDE by mixing together different ratios of 5 low D basis samples, and provided the experimental data for their rheological and mechanical properties. The  $M_n$  of these samples ranged from 47,000 Da to 673,000 Da. At random, 90 of the samples were used as the training set, while the remaining 10 formed the testing set.

A property of interest, p, can be predicted from the MWD of a HPDE sample via the following equation:

$$p = \int f(M)g(M) \ dM \ , \tag{1}$$

where M represents molecular weight, f(M) is a MWD composed of hundreds of data points, and g(M) is the function we want to determine. In practice, the predicted value is obtained by applying weights (in the form of g(M)) to each point on the MWD. However, representing g(M) as a discrete grid would create an unreasonable amount of variables that need to be optimized.

To circumvent this problem, g(M) was constructed using B-splines, so that

$$g(M) = \sum_{i=1}^{N_{\rm sp}} c_i B_i(M) ,$$
 (2)

where  $B_i$  represents the *ith* member of the cubic B-spline basis,  $c_i$  is the associated coefficient that determines the magnitude of  $B_i$ , and  $N_{sp}$  is the total number of splines implemented. As seen in Figure 2, this definition presents g(M) as a continuous function with  $N_{sp}$  B-splines, which is less computationally demanding than solving for hundreds of individual points on a grid. As shown in Eq. (2), optimizing  $c_i$  will produce the best possible g(M).

In order to reduce the  $N_{sp}$  required to sufficiently capture a broad range of MWDs, the molecular weights (M)were scaled to a new domain u such that  $0 < u \leq 1$ . The transformation,

$$u = \frac{M}{M+\beta} , \qquad (3)$$

where  $\beta$  was an optimized parameter found to be 350,000, enabled the implementation of the same B-spline definition and knot vector configuration as shown by Sparrow *et al.*,<sup>16</sup> but with  $N_{sp} = 30$ . Applying the transformation shown in Eq. (3), and substituting Eq. (2) into Eq (1) simplifies to

$$p_j = \int f_j(u) \sum_{i=1}^{N_{\rm sp}} c_i B_i(u) \ du$$
, (4)

where each integer j corresponds to a different HDPE sample. Rearranging the terms yields

$$p_j = \sum_{i=1}^{N_{\rm sp}} \left[ \int f_j(u) B_i(u) \ du \right] c_i \ . \tag{5}$$

The resulting values for  $\int f_j(u) * B_i(u) du$  can be stored in a  $100 \times N_{sp}$  matrix  $\boldsymbol{X}$ , and each  $c_i$  can be stored in an  $N_{sp} \times 1$  vector  $\boldsymbol{c}$ , so that Eq. (5) reduces to



FIG. 2. Two arbitrary g(M) functions created using a B-spline basis, where each  $c_i$  was (a) held constant or (b) allowed to vary. Manipulating the  $c_i$  allows g(M) to take on a wide variety of shapes and structures.

$$\boldsymbol{p} = \boldsymbol{X}\boldsymbol{c} , \qquad (6)$$

where p is a 100×1 vector containing the predicted property value for each sample. The optimal  $c_i$  were determined by generalized Tikhonov regularization; we minimized the following loss function with respect to c:<sup>15,16</sup>

$$L = \left\| \boldsymbol{X} \boldsymbol{c} - \boldsymbol{y} \right\|^{2} + \lambda \boldsymbol{c}^{T} \boldsymbol{A} \boldsymbol{c} .$$
 (7)

The first component of Eq. (7) measures the differences between our predicted values ( $\boldsymbol{p} = \boldsymbol{X}\boldsymbol{c}$ ) and the experimental results ( $\boldsymbol{y}$ ) for each property. In order to find a g(u) that could realistically map an MWD to its properties using this integral model, it was necessary for there to exist a linear relationship between the mean scaled molecular weight  $\langle u \rangle$ , and the property in question. With the exception of Young's modulus, we took the natural logarithm of our properties data in order to meet this criterion.

For the second term of the loss function, the  $\boldsymbol{A}$  matrix was created from the second-derivative finite-difference matrix via the relationship  $\boldsymbol{A} = \boldsymbol{D}^T \boldsymbol{D}$ , which enabled the hyperparameter  $\lambda$  to control the smoothness of g(u).<sup>16</sup> Conceptually, the rows of A can be determined by constructing the second derivative of an arbitrary function of u (e.g., q''(u+nh)) using the limit definition of a derivative. Here n is an integer ranging from 0 to  $N_{sp} - 1$ , and h is an arbitrary constant. As an example, the derivation for the first row of A, which is associated with q''(u), is shown below. First, we must write out q'(u) and q'(u+h):

$$q'(u) = \lim_{h \to 0} \frac{q(u+h) - q(u)}{h}$$
, (8)

$$q'(u+h) = \lim_{h \to 0} \frac{q(u+2h) - q(u+h)}{h} .$$
 (9)

The second derivative of q(u) is determined by

$$q''(u) = \lim_{h \to 0} \frac{q'(u+h) - q'(u)}{h} .$$
 (10)

Substituting Eqs. (8) and (9) into Eq. (10) yields

$$q''(u) = \lim_{h \to 0} \frac{q(u+2h) - 2q(u+h) + q(u)}{h^2} .$$
(11)

Looking at Eq. (11), we see that the coefficients associated with q(u), q(u+h), and q(u+2h) (1, -2, and 1, respectively), are the only nonzero terms in the first row of the  $\boldsymbol{A}$  matrix. This process can be repeated for each n in order to form  $\boldsymbol{A}$ , an  $N_{sp} \times N_{sp}$  matrix. As demonstrated by Eilers *et al.*, penalizing the size of  $\boldsymbol{c}^T \boldsymbol{A} \boldsymbol{c}$  restricts the differences between adjacent  $c_i$ , which is analogous to controlling the second derivative of g(u).<sup>14</sup> These modified B-splines are frequently referred to as P-splines.<sup>14</sup>

As  $\lambda$  increases, the second derivative of g(u) is punished more severely, which forces the function to conform to a straight line. Smaller hyperparameter values permit the presence of more flexible functions that may contain "wiggles." Since most relationships observed in nature can be represented by smooth curves,  $\lambda$  must be optimized (*vide infra*) in order to create the most accurate fit that preserves a physically intuitive shape.

For each property, the optimal hyperparameter  $(\lambda^*)$ was determined via the leave-one-out cross-validation method. As the name suggests, one data point is removed from the training set, while the remaining information is used to create g(u). This function can then be used to predict the property value for the removed data point, and an error is computed. For a given  $\lambda$ , this procedure is repeated until every data point is "left out" once. The  $\lambda$  that produced the smallest mean absolute error (MAE) was considered to be optimal. At the conclusion of this process, each  $c_i$  was re-optimized using  $\lambda^*$  as the hyperparameter, and all 90 training samples as the input data. With g(u) determined for each property, it was then possible to predict the property value for each sample in the testing set. Standard error metrics, including the mean absolute percent error (MAPE) and the coefficient of determination ( $R^2$ ), were used to evaluate the efficacy of our model compared to a polynomial model based on the statistical moments of each MWD.<sup>5</sup>  $R^2$ , which has an upper bound of 1, quantifies how effective a model is at predicting experimental data compared to using the mean of the experimental data for each guess. In other words, it represents the proportion of the variation in the outputs that can be attributed to changes in the input variable. A high  $R^2$  value (interpreted in this work as at least 0.9) is required for a model to be viewed as an effective predictor. The computed errors for both models can be found in Table I.

#### **III. RESULTS AND DISCUSSION**

	Moment	Moments $Model^5$		Integral Model	
Property	MAPE	$R^2$	MAPE	$R^2$	
Low Shear Viscosity	23.3	0.883	15.8	0.955	
High Shear Viscosity	21.5	0.897	11.7	0.972	
Stress at Break	19.5	0.118	10.1	0.678	
Strain at Break	43.2	0.418	30.6	0.081	
Toughness	50.4	0.477	30.5	0.315	
Young's Modulus	8.17	0.354	8.96	0.425	

TABLE I. The computed MAPEs and  $R^2$  values for each property when predicted using a polynomial fit based on the statistical moments of each MWD (see reference 5 for more details), and our integral model.

As shown in Table I, our integral model outperforms the MAPE of the statistical moments model for 5 out of the 6 properties. Although our method performs slightly worse for Young's modulus, the percent errors for the remaining properties all improve by a comparably significant margin. The largest improvement occurs for toughness, whose MAPE is approximately half of that for the polynomial fit. Overall, the integral model vastly augments our ability to accurately predict the properties of HDPE from its MWD.

The integral model also displays improved  $R^2$  values for 4 out of 6 properties. In particular, the increases in the low and high shear viscosity  $R^2$  values to 0.955 and 0.972, respectively, indicate that our model is far more reliable at predicting rheological properties than the previous strategy. However, the  $R^2$  value for each mechanical property is well below 0.9. This indicates that the g(u) functions we create for the stress at break, strain at break, toughness, and Young's modulus are not reliable.

Nevertheless, the promising  $R^2$  values for the rheological properties, and the nearly unanimous improvement in error metrics for every property, indicate that this model is a positive step towards precisely predicting



FIG. 3. The optimized g(M) functions for the (a) Low Shear Viscosity, (b) High shear Viscosity, (c) Stress at Break, (d) Strain at Break, (e) Toughness, and (f) Young's Modulus. Based on the model shown in Eq. (1), the value of g(M) indicates the relative influence that regions of a MWD have on the value of a property.

HDPE properties from MWDs. Furthermore, as more data is added, the accuracy of the integral model should improve, since the relationship between MWDs and properties will become more evident, and therefore be easier to capture and predict.

An additional benefit of implementing an integrationbased model is that the determined g functions can provide insight into how specific components of a MWD influence a property. To facilitate the interpretation of our models, each g(u) was converted back to a function of M by inverting the relationship depicted in Eq. (3). These new functions are displayed in Figure 3. Referring back to Eq. (1), one will notice that g(M) acts as a system of weights on a MWD in order to predict a property value. For instance, as seen in Figure 3a, as the molecular weight is increased to 0.5 MDa, q(M) increases, indicating that adding a 0.5 MDa component to HDPE will increase its low shear viscosity more than mixing in an equivalent amount of 0.1 MDa HDPE. Improvements to the accuracy of each q(M) should eventually enable us to glean more insights into how MWDs influence each property.

#### IV. CONCLUSIONS

By implementing an integration-based statistical model, we were able to predict the properties of HDPE using its MWD. Other methods, which rely on statistical depictions of a MWD such as  $M_n$  and D, are insufficient for analyzing the properties of more complex distributions. The use of B-splines and P-splines allowed for the creation of tunable functions that could be be optimized via generalized Tikhonov Regularization to map the MWDs of HDPE to their properties. We observed significant improvements in MAPEs and  $R^2$  values when our model was compared to a polynomial prediction based on statistical moments.

The introduction of more samples to train on, and the addition of correction terms to account for interactions between different components of a MWD, should further enhance the ability of this model to precisely estimate the properties of HDPE. More complex analytical models, such as Kernel Ridge Regression and Neural Networks, will be constructed to further gauge the efficacy of our procedure. Once a more accurate prediction method is developed, it may possible to use a "learned" function to create MWDs that possess a desired set of properties.

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### EFFECTS OF TEMPERATURE ON RUTHENIUM OXIDE THIN FILMS

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### ABSTRACT

Within this report, experiments were conducted to determine what effects temperature have on thin film composition, crystalline orientation, and roughness. During these experiments the samples were sputtered at different temperatures (100°C, 300°C, 500°C). The properties of the thin films were observed using X-Ray diffraction. It was found that increase in temperature causes an increase in density, and roughness.

Keywords: Thin Film, Sputtering, Deposition, X-Ray Diffractor, RuO2

### **1. INTRODUCTION AND BACKGROUND**

Thin films are used in numerous applications such as alternative energy, optics, architectural glass, etc. making them of great interest. For fabricating thin films, sputtering achieves good sample uniformity and is user-friendly. XRD (X-ray diffraction) is used to determine properties such as composition, crystalline orientation, thickness, and roughness. We plan on investigating what affects temperature has on these properties.

For sputtering, the desired substrate is put into the vacuum chamber and the air is vacuumed out to 8E-6 Torr. Inert gases are pumped into the chamber, these gases are used because they will not react with

the target material. A negative electrical potential is applied to the target, making it a cathode and the surrounding chamber, the anode. Next, the free electrons leave the now negatively charged target and hit the inert gas atoms. This causes the electrons from the inert gas to pull away, making the inert gas atoms positively charged ions. The glow, plasma, seen during the deposition is the free electron reconnecting with the gas ions. Then, the inert gas ions are attracted to the negatively charged target, a collision cascade is seen. The ions accelerate toward the target and sputter off the target material. These atoms move across the chamber and are deposited onto the substrate, as seen in Figure 1.



Figure 1: Sputter Deposition Diagram

### 2. MATERIALS AND METHODS

### Experiments and materials...

- 1. VWR Symphony Sonic Bath: Used to clean substrate in heated acetone solution.
- 2. GloQube Plus Glow Discharge System for TEM Grids and surface modification: used to clean the substrate.
- 3. CMS (Combinatorial Material Science) Series- Advanced Research System utilizing Sputtering or Electron Beam Techniques

manufactured by Kurt J. Lester Company. This was used to make the Ruthenium Oxide thin films at different temperatures.

4. Rigaku SmartLab X-Ray Diffractometer: For thin film characterization.

Ruthenium Oxide thin films were made on glass substrates by magnetron sputtering in Ar and O2. Starting with a clean sample is pertinent to have a good thin film. Poor sample preparation can cause problems with the thin films adhering to the substrate, surface mobility, uniformity issues, etc. With the chosen substrate of glass slides; each sample was cleaned with Acetone in a 10 min heated sonic bath. The substrate is then plasma cleaned reversing its polarity making it hydrophobic. Plasma cleaning with positive polarity on the substrate for 30sec at 30mÅ and the voltage was approximately 400V.

The films were sputtered at a constant rate of  $3.3\text{\AA}/s$  by controlling the power. The substrate was heated to 100°C, 300°C, 500°C for each sample. Prior to deposition, the target was pre-sputtered for 5 minutes to remove contaminates. Each sputter deposition was performed for six minutes. This time results in films approximately 20nm thick, as indicated by a quartz crystal resonance scale. A mass flow controlling system was used to introduce the Ar and the O2 to optimal pressure using the capacitance manometer. The oxygen flow ratio (OFR) was at 50% (Búc et al.).

Once the thin film is made they are put in the XRD machine. XRD is a nondestructive test used to characterize crystalline materials. It works by exposing material to X-rays and measures the angles of the X-ray as it bounces off from each set of lattice planes, elastic scattering. Depending on the distribution of atoms in the lattice the peaks will have different intensities. Since each atom has its own lattice structure the peaks show which material is at the given spot. The machine was set to scan the thin film samples for a duration of 21 min.

### **3. RESULTS AND DISCUSSION**

Other characteristics to look for in a good thin film are: uniformity, absence of cracks, and strong adhesion. This can be done with by using X-ray Diffraction (XRD).

As shown in Figure 2, when an XRD scan was done, peaks of both RuO2 and RuO4 are shown. Looking at the RuO2 peaks at the (110) plane the peak is higher on the films that were sputtered at  $500^{\circ}$ C. This indicates as the temperature increases the thin film has a stronger, more oriented crystal structure. Due to the presence of RuO2 and RuO4 the densities varied during the reflectivity scan of the thin film.

RuO2 has a density of 6.97 g/cm<sup>3</sup> and RuO4 has a density of 3.29 g/cm<sup>3</sup>. Figure 3 and Table 1 show the varying densities, as the temperature was increased during each deposition the density had also increased along with roughness and thickness. Material that is crystalized has a higher density than material that isn't. When the material is deposited on the heated substrate the atoms move around to form crystals which in turn cases the roughness to increase. The drawback of depositing at high temperature is the fact that the film will not be as smooth even though it is more crystalline. Thickness was controlled around 20nm using the quartz crystal microbalance.



Figure 3: Parameter change vs Temperature



**Figure 2:** Ruthenium Oxide Thin Film Scan at different Temperatures **Table 1:** Ruthenium Oxide thin film parameters at different Temperatures

Sample	Oxygen Flow Ratio (%)	Substrate Temperature (Celsius)	Density (g/cm^3)	Thickness (nm)	Roughness (nm)
RuO2/RuO4	50	100	5.55	19.43	0.96
RuO2/RuO4	50	300	6.37	25.27	2.80
RuO2/RuO4	50	500	6.56	20.13	3.68

### **4. CONCLUSION**

In conclusion, we can see that with an increase in temperature of 500°C RuO2 is able to form on a substrate with strong crystalline orientation. Accomplishing the goal of depositing Ruthenium oxide thin film that crystalize in rutile structures. With thin films being used in in multiple fields this information can become vital in how thin films made for their intended purpose.

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### Exploring the Superconducting Phase Boundaries of an NbN Thin Film Ryan Zhang, Anand Kumar Ithepalli, Debdeep Jena

### Abstract

This project experimentally observes trends between critical temperature, field, and current in superconducting NbN thin films. Obtaining a clear picture of the three-dimensional superconducting phase boundary in  $T_c$ - $H_{c2}$ - $J_c$  space will allow for optimized design of applied superconductor technologies. Trends in  $T_c$ ,  $H_c$ , and  $J_c$  were quantitatively measured by taking resistivity profiles and I-V curves at varying magnetic fields and temperatures. These trends were fitted to BCS theory-motivated linear and power law models. Finally, the upper critical field was significantly enhanced by exploiting the parallel field geometry for films thinner than their London penetration depth.

### Introduction

Some materials, when cooled below a critical temperature  $T_c$ , transition into a superconducting phase where electrical resistance drops to zero. First observed in mercury in 1911, superconductivity has since been shown to arise in a wide range of materials, including metals, metallic compounds, alloys, and even nonmetals under high pressures<sup>1</sup>. Along with exceeding the critical temperature, there are two other ways of breaking superconductivity. Applying a strong enough magnetic field or passing a large enough current through the material will destroy superconductivity so long as the critical field  $H_c$  or the critical current density  $J_c$  is exceeded. Furthermore, these three parameters–temperature, magnetic field, and current density– can simultaneously contribute to the breaking of the superconducting state.

As more technological applications of superconductivity are developed, it becomes increasingly important to understand how and when superconductivity is destroyed in various materials. This project focuses on one such material, NbN, and aims to trace out a three-dimensional superconducting phase diagram in  $T_c$ ,  $H_{c2}$ ,  $J_c$  space. NbN is a Type II superconductor with a relatively high  $T_c$  (~16.5 K), making it popular in superconducting electronics circuits<sup>2</sup>.

Knowing how to manipulate and traverse the superconducting phase boundary of various materials is the first step in understanding where these superconducting materials can be applied. Researchers have long tried to increase the T<sub>c</sub> of superconductors, as it is not suitable for most applications to require a liquid-helium cryogenic cooling system. For example, high-T<sub>c</sub> materials in the YBCO family can be cooled by the much more easily attainable liquid nitrogen, allowing for larger scale applications like in zero loss transmission lines. Other technologies such as MRI and NMR rely on a superconductor's ability to sustain large currents and generate intense magnetic fields, which is directly limited by J<sub>c</sub> and H<sub>c</sub>. More specifically, superconducting NbN must survive high-field environments in particle detector applications<sup>3</sup>.

As with any other phase, the superconducting state is no longer thermodynamically favored when it fails to minimize free energy. There is plenty of evidence suggesting the existence of an energy gap separating the superconducting states from the normal states. Experiments show that there is an exponential dependence on 1/T in the heat capacity of superconductors, which is the solution for a two-level system, strongly indicating the presence of an energy gap. Microscopically, BCS theory predicts that the energy gap arises from the pairing of electrons in k-space through the attractive electron-phonon interaction.

Strong magnetic fields break superconductivity by raising the free energy of the superconducting state until it is no longer favored. This is caused by the Meissner effect, a phenomenon of the superconducting phase which expels all magnetic field from the interior of the material. The increase in free energy equals the work needed to set up an opposing field that will cancel out the interior field and thus realize the Meissner effect<sup>4</sup>. The free energy of the normal state remains largely unaffected, as most metals have negligibly small magnetic susceptibility in the normal state.

NbN is a type II superconductor, meaning that it has two critical fields  $H_{c1}$  and  $H_{c2}$ . Below the lower critical field  $H_{c1}$ , the superconductor behaves as though it were type I, with a so-called "complete" Meissner effect. Between the lower and upper critical fields, the Meissner effect is said to be incomplete. In this mixed state, magnetic flux can penetrate the interior of the superconductor in the form of magnetic field vortices that are pinned down by defects. However, electrical resistance remains at zero below the upper critical field  $H_{c2}$ . In type I superconductors, a large enough current may destroy the superconducting state simply by generating a magnetic field greater than  $H_c$ . In type II superconductors, a current larger than  $J_c$  will generate a Lorentz force greater than the flux pinning force, thereby killing the vortex state<sup>5</sup>.

Even in the complete Meissner effect, a small amount of external field penetrates the surface of the superconductor and exponentially decays into the bulk with characteristic length known as the London penetration depth. If a superconducting film thinner than the London penetration depth is aligned parallel to an external field, the field will not fully decay, leading to a much weaker Meissner effect. This slows the increase in free energy of the superconducting state as a function of the applied field. Thus, a much larger field  $H_{c2}$  is needed to break superconductivity in thin films for a parallel field geometry<sup>6</sup>.

### **Results and Discussion**

The  $T_c$ ,  $H_{c2}$ , and  $I_c$  of two NbN films were measured. Both samples were deposited via molecular beam epitaxy onto 6H-SiC substrates and grown to different thicknesses, 3.1nm and 7.8nm. The 7.8nm sample was further processed into wires measuring 180 microns long and 5 microns wide.

The H-T phase boundary of the 3.1nm NbN film was probed by two different resistivity measurement sequences programmed onto a commercial Physical Property Measurement System (PPMS). The first sequence provided a T<sub>c</sub> vs H trend by sweeping temperature at various fields,

and the second sequence provided an  $H_{c2}$  vs T trend by sweeping field at various temperatures. For all phase boundary data that was collected, critical parameters were extracted at the highest value at which resistance fluctuated around zero. Fig. 1 shows the resistivity profiles resulting from both measurement sequences, as well as the linear fit applied in order to further approximate and illustrate the phase boundary. Due to the lack of data points at reduced temperature t=T/T<sub>c</sub> below 0.5, a linear fit was chosen over the more commonly used quadratic temperature dependence model, as it has been shown that the phase boundary approaches linearity as t approaches 1<sup>7</sup>.

The J-T phase boundary was probed in both the 3.1nm NbN film and the 7.8nm processed NbN film. I-V curves were taken at various temperatures, forcing current and sensing voltage. Figs. 2a and 2b show the I-V characteristics slowly taking on the expected linear regime of a normal metal as temperature approaches T<sub>c</sub>. A theory-motivated power law model<sup>8</sup> of the form  $\Box_{\Box}(\Box) = \Box_{\Box}(\theta)(1 - \frac{\Box}{\Box_{\Box}})^{\Box}$  was applied to the critical current data for both films, as shown in Figs. 2c and 2d. The fit for the 3.1nm NbN film predicts a critical current of 38.3 mA at absolute zero and a critical temperature of 10.3K, 3.7% off from the observed value of 10.7K. The I-V data for the 7.8nm processed NbN film could be adapted into critical current density, as the wire dimensions were known. The fit for the 7.8nm NbN film predicts a critical current density, as

I-V curves were also taken at various fields for both samples in an attempt to probe the J-H boundary, as shown in Figs. 2e and 2f. Due to the magnetic field capabilities of the PPMS, the I-V measurements were taken at a temperature close enough to  $T_c$  to ensure that  $H_c$  was below 9T. In this way, the entire J-H boundary can be probed, as the field must be incremented up to  $H_{c2}$  in order to bring  $J_c$  down to 0. A general decreasing trend between critical current and field can clearly be observed, accompanied by a gradual transition into the linear regime. However, superconductivity does not seem to be present for the most part, as nearly every curve immediately departs from the V=0 axis, meaning zero resistance is not observed. Either more measurements or further data analysis is necessary to extract meaningful critical current values against field, as the method of taking the highest value at which the resistance fluctuates around zero fails for these data.

Critical field measurements of the 3.1nm film were taken in both perpendicular field and parallel field geometries in order to observe anisotropy in  $H_{c2}$ , as the film thickness was much smaller than the reported penetration depth of 280 nm to 600 nm<sup>9</sup>. Measurements at 9K and 8K yielded in-plane critical fields about 9 times higher than those measured in the normal perpendicular geometry, as compared in Fig. 3. In-plane measurements at lower temperatures were not possible, as it would push the critical field above the PPMS limit of 9T. This data agrees nicely with studies done on 2D superconductivity in other materials, such as an in-plane  $H_{c2}$  of more than six times the out-of-plane  $H_{c2}$  observed in NbSe<sub>2</sub><sup>10</sup>.

### Figures



**Figure 1.** H-T phase boundary data for 3.1nm NbN film. Dashed lines in (c) and (d) are theorymotivated linear fits applied to the observed data, not model-based predictions. (a) Resistance profiles at increments of 1K, sweeping field. (b) Resistance profiles at increments of 1 Tesla, sweeping temperature. (c) Critical field plotted at seven different temperatures, extracted from (a). (d) Critical temperature plotted at five different fields, extracted from (b).

(a)



**Figure 2.** I-V measurements. Voltage compliance limits vary from 50mV to 200mV, so the normal metal linear regime is not shown at low temperatures and fields. (**a**) I-V curves of 3.1nm NbN film at various temperatures. (**b**) I-V curves of 7.8nm NbN film at various temperatures. Temperature increments decrease near  $T_c$  in order to pinpoint the phase transition with greater accuracy. (**c**) Critical current plotted at eight different temperatures, extracted from (**a**). (**d**)

Critical current density plotted at nine different temperatures, extracted from (b). (e, f) I-V curves of 3.1nm and 7.8nm NbN films at 9K and 6K, respectively, at various magnetic fields.



**Figure 3.** Critical field comparison of 3.1nm NbN thin film in different field geometries. (**a**) Resistance vs perpendicular field profiles at 9K and 8K with upper critical fields of 0.5T and 1.0T, respectively. (**b**) Resistance vs parallel field profiles at 9K and 8K with upper critical fields of 5.8T and 8.0T, respectively.

### Outlook

In the future, this study can be extended in many different directions. To further investigate thin film anisotropy in superconducting properties, critical parameters could be measured for a series of NbN films epitaxially grown to different thicknesses, perhaps between 3nm and 50nm, in order to complete a thickness dependence study. In very thin films where anisotropy is observed, an angular dependence study is very achievable using the rotator accessory for the PPMS, where the angle between the film and applied field is continuously swept and critical parameters are measured. To obtain a more complete in-plane H-T phase boundary, additional measurements should be taken with equipment capable of generating stronger fields, such as the blue 40T PPMS. In the interest of thoroughness, I-V measurements can also be retaken, sweeping current in both directions instead of only in the positive direction. There is also motivation to take further I-V measurements and observe the  $J_c$  vs T trend at higher external fields, in order to study the complex vortex dynamics unique to the mixed state occurring in Type II superconductors. These vortex dynamics could result in more exotic temperature and field dependencies. Finally, further data analysis can be performed in order to get a better estimate of upper critical field, such as extending the maximal derivative dp/dH in the superconducting transition profiles<sup>11</sup>. This method of extracting critical values could possibly be applied to the seemingly unusable field-dependent I-V data to help resolve the J-H phase boundary.

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### **Appendix: Experimental Methods**

The 9 Tesla PPMS from Quantum Design with Evercool-II liquid helium cooling system was used to create a stable magnetic field and thermal environment for electrical transport measurements. Before being placed in the PPMS sample chamber, both the 3.1nm unprocessed sample and the 7.8nm processed sample were mounted onto a standard PPMS measurement puck using low-temperature varnish. Then, the samples were ultrasonically wirebonded to Channel 3 of the puck in a 4-point Kelvin probe configuration for improved measurement accuracy. The ultrasonic power parameter was tuned in order to optimally bond to the NbN surface, as well as the gold pads on the puck. The processed sample presented additional wirebonding challenges, as the 1 sq. µm features were only just large enough to accommodate the aluminum wire without shorting the probe.

Some transport measurements were also directly taken using the built-in resistivity option for the PPMS. The first measurement sequence, which observed the  $T_c$  vs H trend, incremented the magnetic field by 1T from zero field to 9T. At each increment, the temperature was swept from 4K to 20K, taking 5 resistance readings at intervals of approximately 0.25K. The more complete resistance profile up to room temperature was sacrificed in the interest of time. The relatively low number of readings was also chosen for shorter measurement times, since error analysis showed no discernable difference in standard deviation between 5 readings and 25 readings. One factor that increased measurement time was the lag between the actual temperature of the sample chamber and the reported temperature on the PPMS, which was compensated for by programming in long delays after particularly drastic changes in temperature.

The second measurement sequence, which observed the H<sub>c</sub> vs T trend, similarly incremented the temperature by 1K from 3K to 9K. At each increment, the field was swept from zero field to 9T, taking 5 resistance readings at intervals of 0.2T. For the resistance measurement of the 3.1nm unprocessed sample, Channel 3 was configured to force  $100\mu$ A of current in order to avoid hitting the maximum built-in voltage compliance limit of 95 mV. For the in-plane H<sub>c</sub> vs T measurements, a rotator accessory was used that required a separate puck and came with a slightly more accurate temperature sensor. A computer-controlled motor was attached to the rotator accessory in order to precisely manipulate the orientation of the sample. However, there was usually an offset anywhere from 2 to 10 degrees in the motor, which was manually compensated for. The two measurement sequences above could not be successfully performed on the 7.8nm processed sample due to equipment reservation conflicts and instrument malfunctions.

IV measurements were taken via an external Agilent B1500A Semiconductor Device Analyzer which interfaced with the PPMS through triaxial cables. Two medium power SMU modules were used to force current and sense voltage as part of the 4-point Kelvin probe. A compliance voltage of either 50 or 200 mV was set for most measurements in order to prevent the extremely thin wires of the processed sample from breaking. The temperature and magnetic field was then manually incremented without the assistance of a programmed sequence. There was also a significant offset of about 100 mV in the voltage readings as well as considerable voltage noise, which was somewhat mitigated by performing SMU Module Self Calibrations and SMU Zero Cancel Calibrations. Although this led to inaccurate voltage readings, measurement of the critical current was not affected and the transition could still be reported with a great deal of accuracy.