New micromechanics and structure-property connections in biomaterials

1 Introduction and Significance

Structural biomaterials, such as bones, shells, and insect wings, display a fascinating array of sub-micrometer structures (see Fig. 1). These structures endow the materials with *effective*, *new* properties, primarily on account of their geometry and dimensions. The properties are considered *new* because the material composing the structure does not itself display them. The term *effective* implies that the property manifests chiefly at length scales that are much larger than the characteristic length scales of the structure. For example, butterfly wings are decorated with sub-micrometer *scale*-like structures (Fig. 1(a-b)), which endow the wing with stunningly iridescent colors [1]. The material composing the scales, chitin, does not in itself display any of the colors of the wing. The bright colors are only visible when the wing is viewed from length scales that are much larger than the dimensions of the *scale*-like structures.

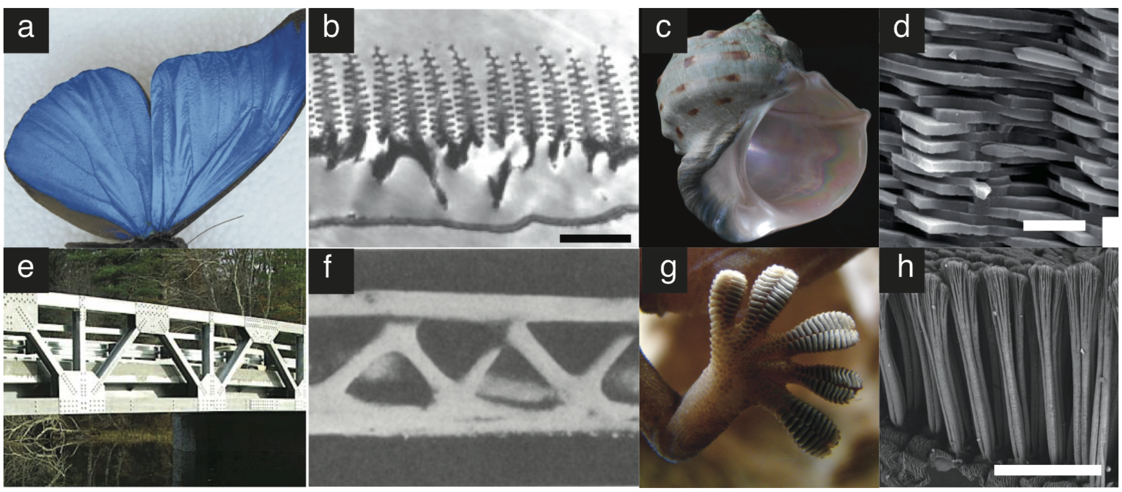

Figure 1: Examples of structural biomaterials with known structure-property connections. (a–b) show a butterfly's wing (*Morpho rhetenor*) and its sub-micrometer structure [1]. (c) shows a molluscan shell (*Turbo marmoratus*), while (d) shows the brick-and-mortar structure of a layer (nacre) of the shell that enhances its toughness [2]. (e) shows a flat Cambridge-style bridge [3], while (f) is the cross-section of a vulture's wing that reveals a similar truss-like structure [4]. (g–h) show a gecko's foot [5] and the sub-micrometer bristle-like structures on it [6]. The scale bars shown in (b), (d), and (h) measure $2\,\mu$m, $5\,\mu$m, and $50\,\mu$m, respectively.

Engineers have independently discovered many structure-property connections found in nature. One example is the truss-like internal structure of bird bones that maintains the bones' stiffness while reducing their weight (see Fig. 1 (e–f)) [4]. However, most structure-property connections found in nature were not anticipated by engineers and have inspired many important new technologies [7, 8]. An example is the hierarchical bristle-like structure found on the feet of geckos (Fig. 1 (g–h)). These bristles enable the gecko to harness *van der Waals* forces to scale walls without the need for any claws or secretions. This discovery in geckos has led to the creation of several new bio-mimetic adhesion technologies, which have been used to create climbing robots [9, 10, 11]. The study of structure-property connections also has the potential to germinate new ideas in the fields of theoretical mechanics (e.g. multi-scale mechanics, composites theory) and applied mathematics (e.g. homogenization theory) by providing new phenomenon to model and explain. Consider again the discovery in geckos, which has led to the development of several new ideas in the field of theoretical contact mechanics, and has completely re-invigorated this classic subject [12, 13].

The PI's long-term research goal is to use experimental and theoretical mechanics techniques to identify new structure-property connections in nature, and understand them quantitatively. The proposed CAREER research is aimed at discovering new structure-property connections in structural biomaterials (SBs). Most SBs are composites in which stiff, mineral-based lamellae (thin plate-like structures) are glued together with compliant, protein-based materials [14]. The proposed research will focus on understanding how this elastically heterogeneous, lamellar structure (EHLS) is connected to the SB's effective strength. The PI has identified the anchor spicules of the marine sponge *Euplectella aspergillum* as a model material system for the proposed investigation. The proposed research is grouped into three sub-projects that will focus on experimental, computational and theoretical aspects of the project as described in sections 3–4.2, respectively.

In addition to the EHLS, the sub-micrometer structures of SBs display a variety of design motifs, such as hollow-truss or porous [15] (feather rachis, bones, skulls, grass), and twisted plywood [16]. However, past and recent experimental work has shown that EHLS correlates with some very interesting mechanics phenomenon, such as strain localization, shear banding, crack arresting, and co-operative motion (esp. slip) of mineral layers [7, 17, 18, 19]. Therefore, EHLS has the potential to affect the material's effective properties in remarkably clever, new ways. Hence, studies involving EHLS can lead to the discovery of interesting new principles in mechanics of materials.

Structural mechanical properties can broadly be classified as either strength-related or toughness-related. Very crudely, toughness defines how successful the material is at limiting the evolution/growth of damage (in the form of cracks and other flaws) once it has initiated. Whereas, strength-related properties define how successful the material is at resisting the initiation of damage itself.

A material's sub-micrometer structure usually affects both toughness, and strength and it is desirable for a material to have both high strength and toughness. Therefore, it is not easy to know whether, in a given SB, the EHLS is connected to toughness or strength. Since EHLS is a result of evolutionary pressures, it is likely to be connected to the property that most critically affects the organism's *fitness*. It is possible that the EHLS is primarily connected to different structural properties in different SBs, however a disproportionate number of structure-property investigations in SBs over the past few decades have focused exclusively on toughness-related properties [14, 18, 17, 20, 21].

The reason for this could be that that the seminal research on structure-property connections in SBs involved toughness-related properties [18, 22]. Toughness is a very important property, since containing damage is a necessary prerequisite for the organism to later heal the damage and return the material back to its pristine condition. However, not all biomaterials can be healed or repaired (e.g. nails and hair). Thus, it is more advantageous to the organism if its SBs that lack a self-healing ability have a high strength, even at the expense of toughness. The PI believes that the disproportionate amount of importance given to toughness has left many important structure-strength connections undiscovered. By focusing on strength, rather than toughness, the proposed research will bring the attention of the bio-mimetic engineering community to the important, yet often overlooked, idea that the sub-micrometer structure in different SBs is likely connected to

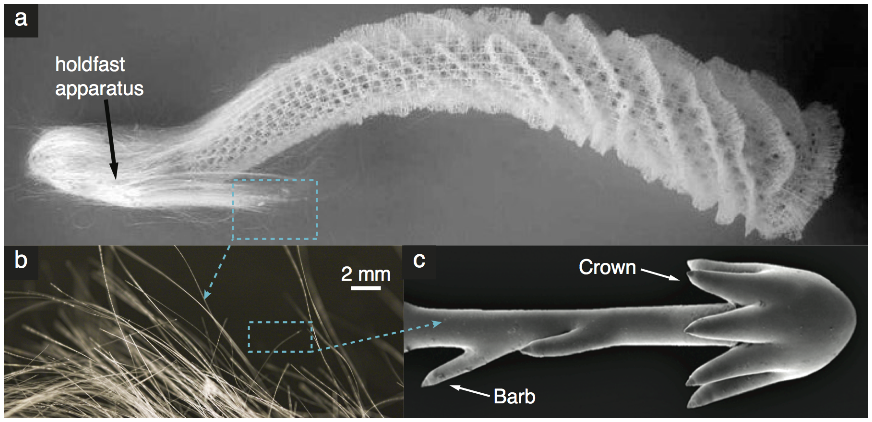

Figure 2: *Euplectella aspergillum* skeleton and spicules. (a) shows an EA skeleton, (b) shows a magnified view of its spicules, and (c) shows a SEM image of the distal end of a spicule.

different properties.

2 *Euplectella aspergillum* as a Model System

For investigating the EHLS-strength connections, the PI has chosen the anchor spicules of marine Hexactinellid sponges as a model material system. The anchor spicules are examples of SBs that lack a self-healing ability. Other reasons for choosing spicules are as follows.

The Hexactinellid sponges, also called glass sponges, are sessile animals of the phylum Porifera. The research will specifically focus on the glass sponge *Euplectella aspergillum* (EA) (Fig. 2), which is found anchored to the sea floor at depths ranging from 25–2000 m [23]. Fossils of Hexactinellid skeletons can be found from as far back as the Cambrian period (500 million years ago) [24, 25]. The fact that this biological class continues to thrive to the present day suggests that it must have developed a number of very successful adaptations in response to evolutionary pressures. In fact, a number of structure-property connections have already been identified in EA [26, 27, 28, 29, 30, 31].

EA is anchored to the sea floor by thousands of anchor spicules (long, hair-like skeletal elements), each of which measures ca. 50 μm in diameter and ca. 10 cm in length (Fig. 2(b)). The distal end of each anchor spicule is capped with a terminal crown-like structure and is covered with a series of recurved barbs that secure the sponge into the soft sediments of the sea floor (Fig. 2(c)). The proximal regions of these spicules are bundled together into a flexible *holdfast apparatus* and cemented to the main vertical struts of the skeletal lattice (Fig. 2(a)). It is clear from the macroscopic shape and arrangement of the spicules that their primary mechanical function is to support the skeleton by transmitting forces from the skeleton to the sediments.

EA's spicules contain an axisymmetric EHLS. Each spicule has a solid silica cylinder as its core, which is surrounded by an array of ca. 10–50 concentric, cylindrical silica layers (Fig. 3(c)). The silica layer thicknesses vary from 1–0.4 μm. A protein-based material glues adjacent silica layers together (Fig. 3 (d–e)) [30, 32]. The simplicity of the EA spicules' EHLS and the clear nature of the mechanical loads that they transmit are important reasons for the PI choosing the EA spicules as the model system for the proposed investigation.

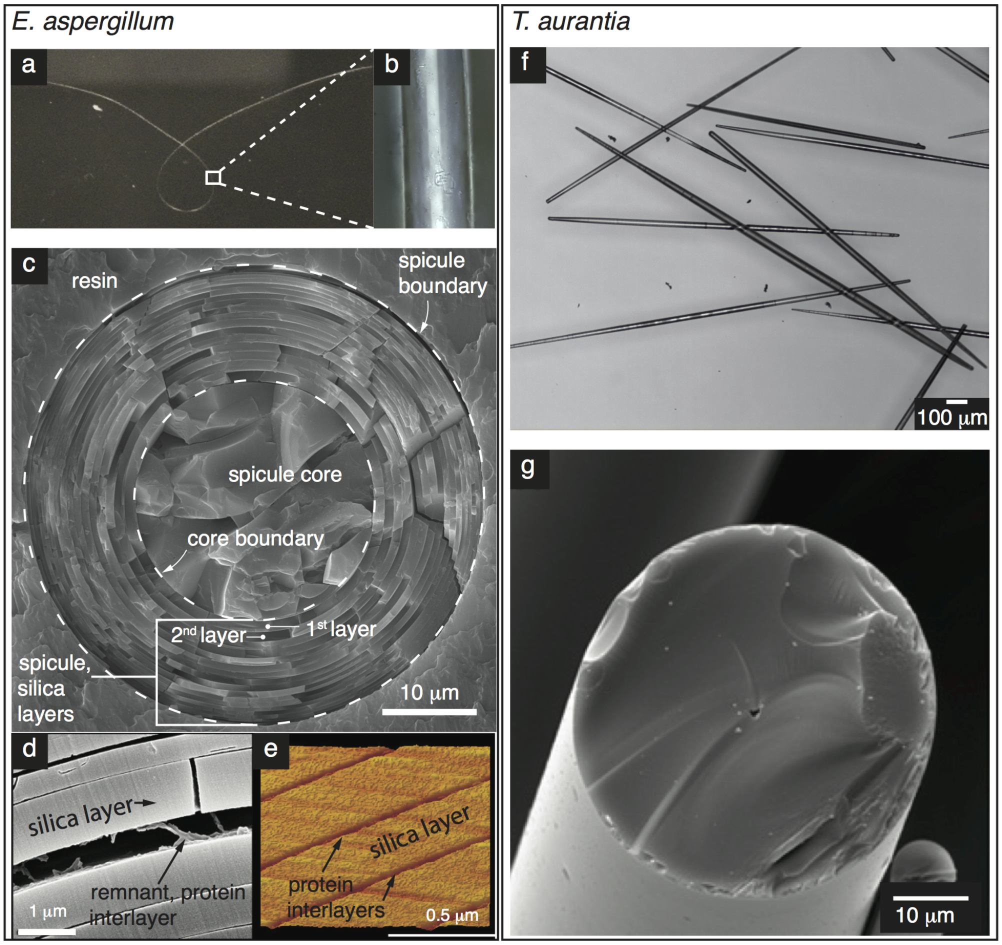

Figure 3: Differences in shape, size and internal structure of EA and TA spicules. (a–e) show images of EA spicules and (f–g) show images of TA spicules. (a) shows an EA spicule. (b) shows a magnified view of an EA spicule's surface. The thickness of the spicule shown in (b) is $\approx 50\,\mu$m. (c) shows a SEM image of a cross-section of an EA spicule that is embedded in a polymer resin and sectioned using a diamond saw. The image reveals at least 15 of the spicule's concentric, cylindrical silica layers. (d) shows a close-up SEM image of spicule's cross-section that was produced by fracturing the spicule [26]. The remnant of the polymer interlayer between the central two adjacent silica layers is marked. (e) shows an AFM scan of a spicule cross-section [26]. The curvilinear, groove-like patterns are the protein interlayers. (f) shows the tapered TA spicules. (g) is a SEM image of a TA spicule's cross-section [31].

3 Proposed Experimental Activities

The PI will use bending experiments to investigate the hypothesis that the EHLS of the EA spicules enhances their strength-related properties. The bending experiments will be supported by Brillouin imaging characterization of the spicules. The Brillouin imaging-related activities will not be discussed here. They will be performed in collaboration with Dr. Kristie Koski, Department of Chemistry, Brown University (letter of collaboration attached).

In the bending experiments, the PI will measure a spicule's bending moment and bending curvature capacities. These are the largest moment and curvature that a spicule can withstand without encountering any damage in a bending experiment. The spicules' moment and curvature capacities are representative examples of their strength-related properties.

There have been some recent experiments that were also aimed at studying the mechanical behavior of glass spicules [33, 34, 35, 36, 37, 38, 28, 31, 39]. These experiments, however, have the following two important shortcomings. (1) In the recent experiments, the mechanical behavior of the glass spicules was compared with that of synthetic glass rods [36, 37, 38]. This is not a good comparison since it is not possible to synthetically replicate the exact chemical composition of the biogenic silica that composes the spicules. Furthermore, recent studies argue that there is also an underlying protein matrix to the silica layers in the spicules [40, 41, 42]. Therefore, the materials composing the glass spicules and the synthetic glass rods, though both based on silica, are different. (2) The EA spicules have a large bending curvature capacity (see Fig. 4). Consequently, the spicules undergo large deformations before failure. However, in recent studies small-deformation mechanics theories were used to interpret the deformation of the spicules. Therefore, the reported values for the spicules' properties are very likely to be inaccurate.

The proposed experiments will address the two shortcomings of the earlier work by comparing the EA spicules with spicules from the glass sponge *Tethya aurantia* (TA) and by using finite-deformation mechanics theories. The TA spicules are also composed of hydrated, biogenic silica [43, 44], and their ^{29}Si NMR spectra is indistinguishable from that of EA spicules (see Fig. 13 in [31]). And the TA spicules are simple homogeneous rods that lack any type of internal structure (see Fig. 3 (f–g)). Therefore, the TA spicules are an ideal control case for the proposed experiments. Comparing EA and TA spicules in the proposed bending tests will clearly delineate the contribution of the EA spicule's EHLS to its strength-related properties.

Some of the challenges inherent to the proposed bending experiments are discussed next. We also present the preliminary results from the bending experiments.

3.1 Bending Experiments

The PI plans to design and build a custom bending test for measuring the bending moment and bending curvature capacities of the EA and TA spicules. The reasons for choosing to build a custom test are the new challenges that are inherent to the mechanical testing of spicules.

Challenges There are a number of new challenges associated with performing mechanical tests on spicules. They arise from the small dimensions of the spicules, the high curvature capacity of the EA spicules, and the tapered shape of the TA spicules. Here we only highlight the challenges that result from the spicules' dimensions and the EA spicule's high curvature capacity.

Bending experiments are routinely used for measuring the mechanical strength of slender structures (beams). However, it is quite challenging to use standard bending test machines in the proposed experiments for the following two reasons that stem from the spicules' small dimensions. (1) The standard machines are primarily meant for macro-scale testing, whereas both EA and TA spicules are only $50\,\mu$m thick and TA spicules are less than 2 mm long. An especially constraining requirement that deters the use of standard devices is that that the indenter's thickness must be much smaller than the span (distance between the supports). (2) For spans in the range of millimeters, it can be estimated that forces of the order of tens of mN will be needed to break the EA spicules. This implies that forces must be measured with at least $\sim 50\,\mu$N resolution. However, the resolution of load cells on standard machines is typically greater than 10 mN [45]. The atomic force microscope (AFM) can easily measure forces with nN resolution. However, typical AFM cantilevers cannot sustain the tens of mN forces needed to break the spicules. For example, the maximum forces silicon and silicon nitride AFM cantilevers can sustain lie in the 2–7.5 mN range [46, 47].

A pilot version of the apparatus has already been constructed and was used to gather preliminary data. It is capable of applying forces greater than 30 mN and has a force resolution less than 20 μN. Briefly, the apparatus performs a type of three-point bending test. Details of the configuration can be found in [48, Ch. 3.1]. The spicules are suspended across a trench and an indenter pushes at the spicule's mid-span cross-section until the spicule breaks. The mid-span is the vertical plane located midway between the trench edges that support the spicule (shown marked in Fig. 4). The indenter is supported by a cantilever, whose deflection is measured by an optical sensor and converted into force. This cantilever-based indenter design is similar to an AFM and has been used in a number of micro- and macro-scale mechanical testing studies [49, 50].

Due to the EA spicules' large curvature capacity it is difficult to measure their strains using the procedures that are employed in standard bending experiments. Strains in standard bending experiments are determined using elementary beam theories, such as Euler-Bernoulli (EB) beam theory [51]. Such theories are based on several assumptions, one of which is that the deformations (strains + rotations) inside the beam are small ($\ll 1$) during bending. However, because of the spicule's large curvature capacity, the rotations of the spicule cross-sections before failure will be much greater than what are admissible for elementary beam theories to apply.

The PI plans on circumventing the problem of large rotations by measuring the geometry of the spicule midline from optical micrographs and then computing the strains from the curvature of the midline. The midline is similar to what is termed the *neutral axis* in beam theories, it is shown marked in Fig. 4. Given that the span-to-thickness ratio is large, large rotation beam theories such as the Euler-Elastica [52, Ch. 19] can be used to compute a homogenous beam's internal strains from its midline geometry.

As part of the proposed research, the PI plans on developing computer vision-based procedures for automatically capturing information about the geometry of the deformed configurations from optical micrographs. The procedures will be based on the *active contours* image processing technique [53, 54]. This technique is currently widely used in the computer vision field for tasks such as motion tracking [55, 56] and stereo matching [57, 58]. Spicule midlines that were automatically identified using a pilot version of the proposed computer vision procedures are shown in Fig. 4 (a–b). Different strain measures can be computed numerically from the captured geometry information. For example, numerically computed curvature values of the identified midlines are shown in Fig. 4 (c). On completion of the proposed computational models, it would be possible to convert information about the spicule's geometry in the deformed configuration, such as the one shown in Fig. 4 (a–b), into information about the spicule's internal strains. That strain information will be used to further test the PI's hypothesis concerning EHLS-strength connections.

Preliminary Results In the proposed bending experiments, the bending moment transmitted across the spicule cross-section varies along the spicule's length. However, the largest bending moment is transmitted across the spicule's mid-span cross-section. Fig. 5 (a) shows preliminary measurements of the bending moment at mid-span, M, as a function of the deflection of the spicule mid-span cross-section, δ. The moment capacity of each of the spicules is the largest value of M in their respective M-δ measurements.

There is a large variation in moment capacities even between spicules belonging to the same species. This is due to the fact that the moment capacity of a spicule strongly depends on its thickness. Because of this, it is difficult to compare the moment capacity of the EA and TA spicules from Fig. 5 (a) alone. From the PI's preliminary theoretical work related to the proposed research

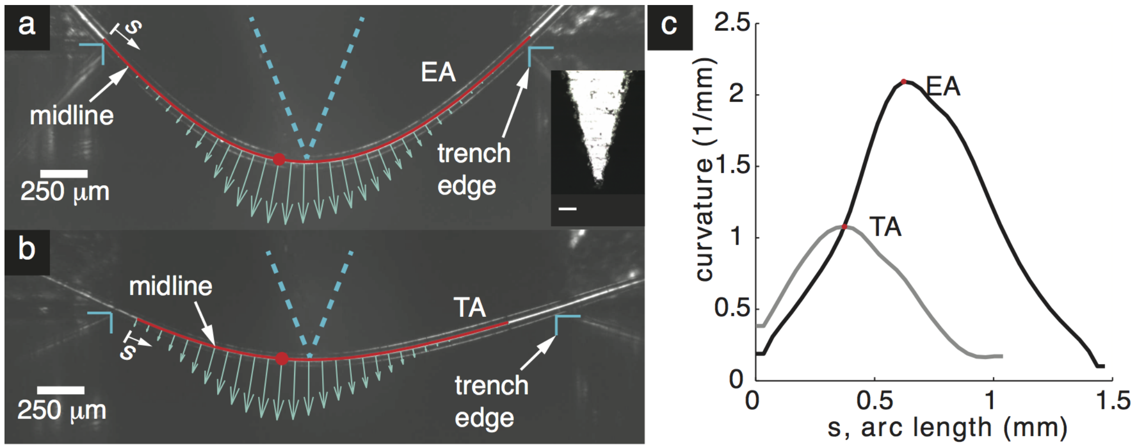

Figure 4: Micrographs from preliminary bending tests on (a) EA and (b) TA spicules. Both (a) and (b) are taken just prior to failure. The cyan wedge depicts the indenter tip. The inset in (a) shows the profile of the indenter tip, with scale bar of 100 μm. The red curves along the spicules' lengths denote the automatically identified spicule midlines. The arrows are normal to the midline curves and scaled by the local curvature values. (c) shows the variation of the midline curvatures along the lengths of the spicules.

(some details are given in section 4.2), it follows that the moment capacities scale as Ea^3 for beams with circular cross-sections. Here, a is the radius of the beam and E is the Young's modulus of the beam's mineral phase. This result holds irrespective of whether the beam is homogeneous or has an EHLS. Therefore, the moment capacities of the different spicules can be compared directly by non-dimensionalizing them using the factor Ea^3. The dimensionless bending moment M/Ea^3 curves are shown in Fig. 5 (b). It can be seen in Fig. 5 (b) that the dimensionless moment capacity of the EA spicules is greater than that of the TA spicules. This result supports the primary hypothesis underlying the proposed research that EHLS contributes to strength-related properties.

The PI's hypothesis involving EHLS also implies that the curvature capacity of EA spicules should be greater than that of the TA spicules. Curvature measurements taken on a single pair of EA and TA spicules indeed support this prediction. Automatically identified spicule midlines are shown in Fig. 4 (a–b). Numerically computed curvatures of these midlines are shown in Fig. 4 (c). Since the images shown Fig. 4 (a–b) were taken just prior to failure, the results shown in subfigure (c) imply that the curvature capacity of the EA spicule is larger than that of the TA spicule. Here, the curvatures can be compared directly since the spicules shown in Fig. 4 (a–b) had similar thicknesses (37 and 40 μm, respectively).

4 Proposed Computational & Theoretical Modeling Activities

As discussed in section 3.1, the preliminary results from the bending experiments show that the EA spicules can withstand greater bending moments than the TA spicules before the initiation of any type of damage. Many more bending experiments and additional checks must be performed before these results can be confirmed. However, the results are quite encouraging since they support the PI's primary hypothesis that that the EHLS enhances the material's effective strength properties. The PI will use a synergistic combination of computational mechanics simulations and experimental activities to determine the precise mechanism(s) through which the EHLS enhances the spicule's strength. The PI will use rigorous, theoretical mechanics techniques to cast the understanding

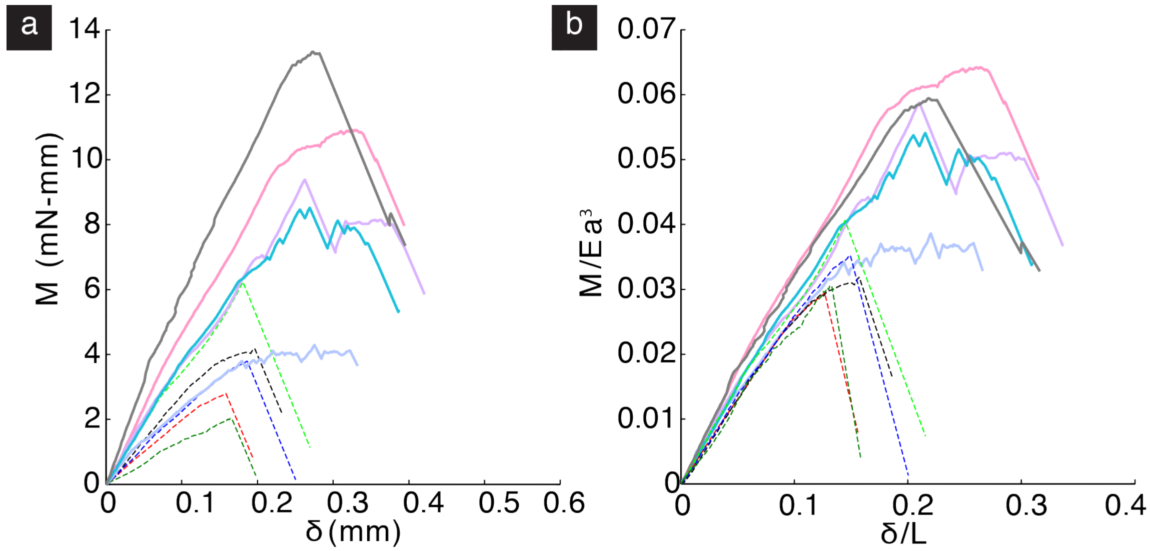

Figure 5: Mid-span bending moment (M) vs. deflection (δ) measurements in 5 EA and 5 TA spicules. (a) and (b) show raw and dimensionless M-δ curves, respectively. Each curve corresponds to the bending test of an individual spicule, while EA and TA spicules are differentiated by the use of solid and dashed lines, respectively.

gained about these mechanism(s) in a compact, quantitatively precise form. Initially, the modeling efforts will be aimed at deriving a high-quality, reduced-order structural mechanics model that is capable of predicting the spicule's strength given the number of mineral layers, the spicule's external and internal geometry, and the elastic properties and strength of the bio-silica in the spicule. The ultimate goal of the theoretical modeling is to arrive at a micromechanics theory, in the form of a set of nonlinear differential equations, for describing the effective mechanical behavior of the spicules before failure.

The strength of materials is often much smaller than the theoretically predicted values [59, 60]. Many explanations have been put forward for this observation [61, 62]. The PI will draw on the following explanation to formulate his conjecture on how an EHLS can enhance a material's strength. Defects (cracks, voids, etc.) greatly reduce the strength of materials from the theoretically possible values [63, 64, 65]. Since defects are stress/strain concentrators, they increase the material strains in their immediate vicinity to several times that of the far-field strain values. For example, linear elasticity theory predicts that the peak strain in the vicinity of a circular hole in a large plate is three times greater than the far-field applied strain. Therefore, failure begins at the material in the immediate vicinity of the defects. At failure initiation, the strains in the material lying in the defect's immediate vicinity are equal to the theoretical strength values, whereas the strains applied to the material far from the defects are much smaller than the theoretical values. These far-field, small, applied strains are what are taken as the material's *true strength*.

The PI has the following conjecture regarding how the EHLS enhances the spicule's strength. In materials with an EHLS, the mineral phase is often very weak in tension [66] and is therefore expected to fail before the protein phase or the mineral-protein interfaces. The PI believes that the EHLS enhances a material's effective strength by making the tensile strains in its mineral phase more homogeneous, especially in the vicinity of defects. At failure initiation, the strains in the mineral phase lying in the defect's immediate vicinity are again equal to the theoretical strength values, however in this case the strains applied to the material far away from the defects are much closer to the theoretical strength values because of the EHLS's homogenization effect. Consequently, the *true strength* in this case is higher. The *strain homogenization* in the mineral phase takes place by the concentration of finite strains in the protein phase, which allows adjacent mineral lamellae to have finite slip-type motion with respect to each other. The concentration of finite strains in the protein phase is a natural consequence of the elastic heterogeneity.

The strain homogenization conjecture is motivated by the PI's preliminary theoretical and computational modeling work on investigating EHLS-strength connections in spicules, experimental observations of shear band-type deformation patterns in nacre [19], and published research in which the shapes of biologically-formed structures (e.g. trees, claws) are explained using the *axiom of uniform stress* [67, 68]. The PI will rigorously test the strain homogenization conjecture by building and studying computational and theoretical mechanics models of EA spicules.

4.1 Computational Modeling

Both computational and theoretical models will be based on a continuum mechanics description of material and interface behavior. The computational models will be solved using numerical techniques, such as the finite element method [69]. Initially, the computational simulations will be used to investigate the *strain homogenization* conjecture put forward in section 4. The preliminary results presented here are an example of such a simulation.

Challenges In both the computational and theoretical models, the mineral phases will be represented as continuum solids [70]. For example, in the preliminary results presented here, the silica layers in the spicule are represented as linear elastic, isotropic solids. Representing the protein phase is, however, more challenging. A direct finite element model could be one in which the protein phase is also represented as a continuum solid. However, such a direct model would be impractical for the following reason.

Due to the high aspect ratio of the protein regions (nm thin, μm long), the data sets in the direct model would be very large. It is possible to use supercomputers to reduce the solution time. However, the PI plans on using the computational models as tools to discover the mechanism(s) involved in the EHLS-strength connection. This requires him to solve the computational models repeatedly as he refines his conjectures. Even though supercomputers may reduce the solution time, using direct finite element methods would still be impractical considering the user time and effort required for transferring, processing and analyzing the large data sets at each iteration.

The PI is currently working on a computational model in which the protein phase is not included explicitly. Rather, its effect is included in the form of a contact law between the mating surfaces of adjacent mineral lamellae. The preliminary results were generated using such a model.

Preliminary Results In the spicule, the silica layers are cylindrical and concentrically arranged. Consequently, if the protein layers allow adjacent silica layers to slip with respect to each other, then the strains in the bending deformation of the spicule will be 3D and complex. A simple 2D spicule model was first studied in order to gain a preliminary understanding of the potential mechanisms through which the protein layers affect the spicule's internal deformation. In the 2D model the silica layers are modeled as thin rectangles whose stress-strain behavior is modeled using plane-strain linear elasticity. The rectangles are stacked on top of each other (see Fig. 6 (a)). As mentioned earlier, the protein layers are not included explicitly in the model. Only their effect is modeled by allowing mating surfaces of adjacent rectangles to slide over each other without friction and without losing contact. A virtual bending experiment was performed on the 2D spicule model using ABAQUS finite element software [71].

A material point was assumed to fail if the tensile strain component in any direction exceeded a certain critical value. The largest tensile strain components were found to occur in the x_1 direction at multiple points on the spicule's mid-span cross-section (marked in Fig. 6 (a), which also shows the x_1 and x_2 directions). The strains on the spicule mid-span in the x_1 direction, ϵ_{11}, are shown in Fig. 6 (b) for the cases of one, two and twenty layers just prior to failure. For the case of one silica layer the computed ϵ_{11} matched well with that from EB beam theory; it varied linearly as a function of x_2. For the cases of greater than one layer ϵ_{11} varied in an interesting, piecewise linear manner as a function of x_2. The strains were linear in each silica layer, but had finite discontinuities across the silica layer interfaces. In effect, the strain became increasingly uniform across the spicule cross-section as the number of layers was increased. This result supports the strain homogenization conjecture that was put forward in section 4.

Fig. 6 (c) shows the curvatures of the spicule midlines (marked in Fig. 6 (a)) for the cases of one, two, and twenty layer(s) just prior to failure. The maximum curvature of the twenty-layer model was 15 times greater than the curvature of the one-layer model. This simulation result is qualitatively consistent with the experimental result reported in Fig. 4 (c) where the curvature capacity of an EA spicule was seen to be ≈ 2 times greater than that of a TA spicule. Recall that the EA spicule contains ~ 25 layers, whereas the TA spicule is homogenous, i.e. it contains a single layer.

4.2 Theoretical Modeling

The reduced-order models will be similar to the computational models described in section 4.1. The important difference is that the deformation of the spicule in the reduced-order models will be assumed to have a simple mathematical form with a tractable number of free parameters. The free parameters will be determined by the boundary conditions using variational principles [72], such as the *principle of minimum total potential energy*. This methodology is often used in structural mechanics for deriving reduced-order models of structures, such as beams and plates. In traditional derivations the deformations are always assumed to be continuous. In the proposed reduced-order models, however, the deformation fields will be allowed to be discontinuous across the interfaces of adjacent silica layers. This is equivalent to allowing the surfaces of adjacent silica layers to slip with respect to each other in the computational models.

Preliminary Results In a preliminary version of the reduced-order model, the silica layers were modeled as a co-axial assembly of annular cylinders whose mating surfaces freely slip with respect to each other. In the preliminary computational results, the strain variation had the following two features. (1) The strains ϵ_{11} varied linearly within each of the silica layers. (2) The peak value of ϵ_{11} in each silica layer was the same. By incorporating these two features as assumptions, the reduced-order model predicts that in a spicule with n silica layers, the bending moment capacity is equal to $\pi E a^3 \epsilon^f \mathcal{M}^n[\boldsymbol{\rho}^n]/4$. Here, a is the spicule's outer radius, E and ϵ^f are the Young's modulus and tensile failure strain of the spicule's mineral phase respectively, and $\boldsymbol{\rho}^n = a(\rho_1^n, \ldots, \rho_{n-1}^n)$ is the set of outer radii of the spicule's silica layers. The details of the non-dimensional, scalar-valued function $\mathcal{M}^n[\boldsymbol{\rho}^n]$ are not provided here.

Using optimization theory and mathematical analysis it can be shown that the maximum value of $\mathcal{M}^n[\boldsymbol{\rho}^n]$ is equal to 4/3. This result implies that the EA spicule's bending moment capacity can be, at most, 33.33% greater than that of the TA spicule. This prediction is broadly consistent

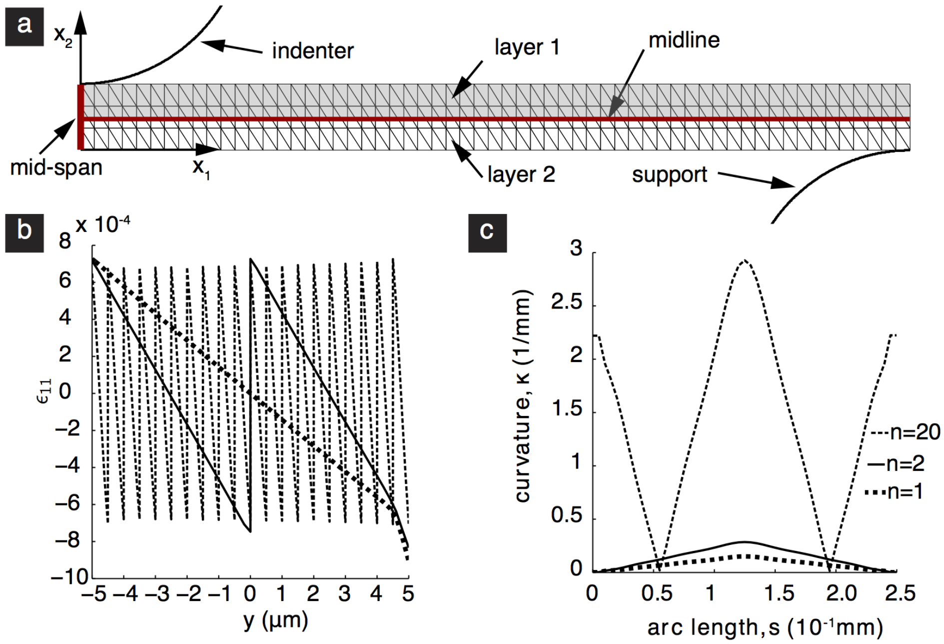

Figure 6: (a) shows the geometry of the computational 2D EA spicule model, for two layers. Only half of the spicule is modeled with symmetry boundary conditions imposed at the mid-span (marked in (a)). (b), (c) show simulation results from one, two, and twenty layer models. In all of the simulations, the length and thickness of the spicule were 250 μm and 10 μm, respectively, and the Young's modulli and Poisson's ratios of the silica layers were 69 GPa and 0.2, respectively. In each of the simulations, the indenter (marked in (a), radius 25 μm) was displaced in the $-x_2$ direction until the maximum value of ϵ_{11} (see text for definition) on the midspan reached the critical value of 0.007. (b) shows the variation of ϵ_{11} on the midspan and (c) shows the variation of the midline (marked in (a)) curvature (un-signed) along the spicule length in the final deformed configuration.

with the experimental results reported in section 3.1, specifically Fig. 5 (b). Furthermore, it was found that in the radii sequence at which $\mathcal{M}^n[\rho^n]$ is maximized, the silica cylinders become progressively thinner from the spicule's core to its periphery. This prediction is also consistent with experimental observations. The PI, in collaboration with James Weaver, Wyss Institute of Bio-inspired Engineering, Harvard, has measured the thicknesses of silica cylinders in over 100 spicules taken from four EA skeletons. The PI found that in almost all of the spicules the overall trend in the silica cylinder thicknesses is that they decrease from the spicule's core to its periphery.

5 Integration of Research and Education

The PI plans on integrating his research and educational programs through a broad range of educational outreach activities, teaching, curriculum development, and student mentoring activities. The details are as follows.

5.1 Educational Outreach

Collaboration with The Sci-Toons Initiative The PI will collaborate with the Sci-Toons initiative at Brown to create scientific cartoons on topics related to bio- and nature-inspired engineering. Please see the attached letter of collaboration from Dr. Oludurotimi O. Adetunji, Director of Brown's Science Center Outreach. The Sci-Toons initiative is an informal science education program at Brown University's Science Center. Sci-Toon videos combine art, animation, high-quality multimedia and storytelling. In the Sci-Toons collaboration, the PI and his students will work with both STEM and non-STEM students, as well as animators in the development of the script, storyboard and science animation. Sci-Toons videos are a powerful tool for engaging and communicating scientific research and concepts to a broad audience. Through the effective use of jargon-free language and engaging storytelling, the Sci-Toons videos aim to get non-STEM majors interested in STEM subjects, STEM majors to appreciate the importance of scientific communication, and the general public to develop a greater understanding and appreciation of science. The Sci-Toons are distributed via a variety of social media platforms.

Through the collaboration, the PI will help create two Sci-Toon videos per academic year for the next five years. The collaboration on the first video will begin in Fall 2014. The first video is tentatively titled "How Natural Evolution Is Helping Engineers." The video will discuss how the idea of "survival of the fittest" results in biological structures/materials acquiring better and new properties through the accumulation of beneficial changes in their macro- and micro-scale structure. The video will discuss some of the close to optimal designs found in nature, and will give concrete examples of how those designs have inspired engineers and inventors (e.g. Velcro, Chipper Chain [73]). The video will end by highlighting the fact that the vast majority of nature's designs remain unknown to engineers, and excite the viewers about the immense possibilities that the discovery of such designs would create for science and engineering.

The Sci-Toon creation group consists of both STEM and non-STEM students and faculty. Funds to support the PI's collaboration with the Sci-Toons initiative are requested as part of the budget (see Budget). The impact of the Sci-Toon videos will be gauged by monitoring the number and geographic distribution of the views that the videos generate. Some of the past Sci-Toons videos have been viewed in over 70 countries. Examples of completed Sci-Toons can be viewed on the Sci-Toon YouTube channel at [74], and more information on the Sci-Toons initiative can be found at [75].

Nature's Ingenious Designs (NID) Competition and Podcast The PI will also post the Sci-Toons videos on his lab website. The website will be set up such that the viewers can post comments and questions about the videos. These comments and questions will be discussed and answered in the NID podcast described below.

The Sci-Toon videos will encourage the viewers to participate in the NID competition that will be started by the PI in Fall 2015. As part of the competition, the participants will be asked to identify a biological construction (material or structure) that displays a strong potential for the discovery of new engineering designs or principles. The participants will be asked to submit a 3–5 minute video clip in which they make their case for why the biological construction that they have identified is a good candidate for conducting investigations related to bio-mimetics.

The NID competition is aimed at addressing a critical bottleneck faced by the bio-mimetics community. There has been interest in the subject of bio-mimetics for the past several decades; however, bio-mimetics has not matured as an engineering subject. The PI believes that identifying good candidate biological materials/structures for conducting bio-mimetic investigations is the critical bottleneck holding back the advancement of bio-mimetics. Historically, in most cases of bio- and nature-inspired discoveries, the designs/principles were recognized in the biological systems primarily by chance (consider again the examples of Velcro or the Chipper Chain [73]). There is currently no protocol for identifying good candidate biological materials/structures for conducting biomimetic investigations. The PI believes that organizing the NID competition would contribute to the creation of such a protocol.

The final discussion session in which the top three winning entries are selected will be recorded and aired as a NID podcast. The winning entries will be awarded a cash prize. The competition results, links to the podcast, and the wining videos will all be posted to the PI's website that hosts the original Sci-Toon video. Funds for organizing the NID competition and podcast are requested as part of the budget.

Collaboration with Brown Science Prep (BSP) The PI will collaborate with BSP to mentor public high school students. Please see the letter of collaboration from Dr. Oludurotimi O. Adetunji. The BSP's mission is to show public high school students the excitement of science through lessons geared towards real-world phenomenon, applicable learning, hands-on demonstration, and experimentation. The lessons are taught by a small group of Brown students. The BSP runs every Saturday for ten weeks every semester on campus, and attendance ranges from 30–40 high school students per semester. The students are from different high schools from across the state of Rhode Island and are usually from communities that consist of underrepresented minorities in STEM fields.

The PI will give at least one lecture to the BSP students every semester. The lectures are tentatively planned to be on topics that introduce mechanical engineering to high school students. Through the use of some concrete case studies, the PI will highlight how the tools developed by mechanical engineers satisfy critical needs in society. An example case study could be how robots are being used by medical professionals, firefighters, and military personnel to save lives.

The BSP students will be invited to visit the PI's lab once every academic year. On the lab excursion day, the PI and his students will show the research being conducted in the lab to the BSP students and explain the operating principles behind the different equipment used in the lab. The PI will also host a BSP student in his lab to work on a project related to the proposed research every summer.

Collaboration with SPIRA SPIRA is a four week camp hosted by Brown every summer for high school age girls to explore engineering. The PI and his students will collaborate with SPIRA in order to encourage young women to pursue education in STEM fields by exposing them to interesting applications of engineering. The camp is free to those who attend and often attracts students from underrepresented minorities. The graduate student engaged in the proposed research (Max Monn) has already been collaborating with SPIRA for the last two years as an invited speaker. His presentations and discussions have focused on the importance of bio- and nature-inspired materials to the future of mechanical engineering. Over the course of the proposed project, the PI will help Max Monn design new activities for the SPIRA participants that will highlight the important topics of structural optimization and biomaterials. An activity under development is the egg drop competition. In the competition the participants are asked to construct an optimal structure for cushioning the fall of a dropped egg by taking inspiration from nature.

Collaboration with Leadership Alliance (LA) In collaboration with LA, the PI will mentor a college student belonging to a group that is an underrepresented minority in the STEM fields. Please see the attached letter of collaboration from Dr. Medeva Ghee, Executive Director, LA. Leadership Alliance, an over 20-year-old consortium of top national universities and colleges, is dedicated to increasing the participation of underrepresented minorities in STEM related graduate programs. LA is conveniently headquartered at Brown and will provide the infrastructure for attracting and recruiting students. The PI will recruit one student every summer through the LA to work with him on a research project that is related to his proposed CAREER research. The PI's collaboration with the student will be one-on-one. He will impart both theoretical knowledge and practical training in academic research to the student. The PI will also provide the student with the guidance and support needed to prepare competitive applications to graduate schools. The student will make either an oral or a poster presentation of the research conducted in collaboration with the PI at the LA National Symposium. Funds to support the LA student in the PI's lab are requested as part of the budget.

5.2 Curriculum Development and Teaching

The PI regularly teaches both undergraduate and graduate courses at Brown. The PI draws on his research to construct motivational examples and design end-of-semester projects in his courses. For example, he uses the close to optimal shapes of biologically formed structures, such as beehives and trees, to motivate the topic of *Calculus of Variations* in his courses. As another example, a junior student in the PI's course "Advanced Engineering Mechanics," researched and presented on the topic "The Optimal Profile of Claws and Talons" as part of her course project. The PI designs his courses such that the students get ample training in critical thinking and he encourages them to initiate and take part in classroom discussions, with the philosophy that no question is too simple or elementary. As a result, several students have expressed interest in joining the PI's lab as undergraduate student researchers. For example, a student, who took the PI's course on advanced engineering mechanics as a junior, will begin working in the PI's lab in Fall 2014 on a topic related to the proposed research.

The PI will develop a new course at the undergraduate level to attract students to engineering. The course will be titled, "How Engineers Think: An Introduction to Modeling." A segment of the course will involve using back-of-the-envelope mechanics calculations to explore size, form, and function relationships in SBs. Example systems for study will include mammalian bones, eggshells, gecko feet and the venus fly trap. These structure-property connections will then be naturally extended to bring out the advantages of engineering at the micro- and nano-scale, especially for innovating the fields of medicine and the life sciences. The goal of the course is to make the students aware of the wide range of exciting opportunities that are only recently becoming available to engineers, and through this awareness attract a more diverse cohort of students to engineering.

5.3 Research Training and Mentoring

The PI is currently advising two Ph.D. students (Max Monn and Kaushik Vijaykumar). The PI recently graduated a master's student (Tianyang Zhang). All their thesis topics are related to the proposed research. The PI collaborated with a Brown undergraduate student (Jarod Ferriera) last summer. The PI's graduate students, principally Max Monn, generated the preliminary results presented in this proposal. Jarod actively participated in the fabrication of the bending apparatus and will be continuing as a new master's student with the PI in Fall 2014. Funds to support Max Monn are requested at part of the budget.

The PI's research training and mentoring style mirrors that of his teaching (see section 5.2). The PI interacts with his graduate students almost daily through one-on-one discussions. The PI welcomes discussions on all topics related to the graduate students' research and maintains an open door policy. The students are provided rigorous training in the research methodology and in a number of research technical skills. They are also provided training in scientific writing, oral presentation, and teaching techniques. For example, the students are encouraged to give oral presentations in the lab group meetings and to serve as Teaching Assistants in the courses taught by the PI. The students are encouraged to think about the relevance and usefulness of their research for solving societal problems and to appreciate the importance of communicating science to an audience broader than the scientific community. As the students progress in their respective programs, the PI will take active part in their placements and will help them integrate into the wider scientific community by providing them with the necessary guidance and support.

6 Broader Impact

Bio-inspired engineering holds tremendous potential for providing great benefits to society. Designs in engineering are usually improved through an iterative incremental process and arriving at completely new designs is slow and expensive. Discovering and studying nature's design solutions provides a new and efficient strategy to arrive at designs that are radically different from and better than existing ones. The proposed research has the potential to lead to the development of new bio-inspired composite materials that have much higher strength to weight ratios compared to today's engineering materials. Such materials will have a wide impact on society by leading to improvements and innovations in a variety of industrial sectors. For example, they will improve fuel efficiencies and safety standards in the transportation (automobile and aviation) and energy sectors. They will also improve the effectiveness of protective structures and gear such as helmets, body armor, and blast-resistant clothing.

The computer vision-based deformation measurement tools that will be developed as part of the project will be of broad generality. The PI believes that they will prove to be very valuable and transformative in the wider experimental mechanics and physics communities, and therefore will have an impact on the civil, mechanical, and aerospace engineering disciplines. The PI and his students will try to proactively disseminate the computer vision-based tools to the wider scientific community.

The PI strongly believes that everyone should have an opportunity to experience the excitement of science and has planned a broad range of outreach activities. The proposed research has strong links to the subjects of patterns in nature, and evolution through natural selection, which generally attract wide public and student interest. The PI plans to draw on these subjects and the subject of bio-inspiration, which is the primary theme underlying the proposed research, to reach people from all backgrounds and excite in them an interest and appreciation of science and engineering. This goal will be pursued through a wide range of outreach activities (see section 5 for details). Some of these activities (collaborations with LA, BSP, SPIRA) are targeted at specific student groups and focus on underrepresented minorities in science and engineering, while others (Sci-Toons, NID competition, and podcast) have a more global scope.

Through his educational and research mentoring program at Brown, the PI plans to train and encourage his students to be not just technically brilliant scientists but also creative thinkers who care about societal problems.

7 Prior NSF Support

None.