Differential multiscale modeling of chemically complex materials under heavy deformation: Biological, bioinspired and synthetic hierarchical materials

**Abstract**

This research was focused on modeling and design of high stress and impact mitigating structures, utilizing nanoscale patterning and hierarchical biomimetic concepts. The eventual goal is to create heterogeneous, hierarchical designs for thin coatings and bulk materials, capable of providing enhanced ability to mitigate high rate impact and deformation. The potential of a structure to mitigate impact, large stress and large deformation is characterized by (i) the ability of the material to dissipate energy under high rate deformation, (ii) the resistance to...
Differential multiscale modeling of chemically complex materials under heavy deformation: Biological, bioinspired and synthetic hierarchical materials

ABSTRACT

This research was focused on modeling and design of high stress and impact mitigating structures, utilizing nanoscale patterning and hierarchical biomimetic concepts. The eventual goal is to create heterogeneous, hierarchical designs for thin coatings and bulk materials, capable of providing enhanced ability to mitigate high rate impact and deformation. The potential of a structure to mitigate impact, large stress and large deformation is characterized by (i) the ability of the material to dissipate energy under high rate deformation, (ii) the resistance to brittle fracture by crack formation under high rates, and (iii) the ability to redistribute load underneath a thin external coating film. To achieve this, our efforts are centered on the development of a holistic atomistic based core model of the deformation and fracture mechanisms of thin nanostructured coatings. Using atomistic simulation, we study the behavior of nanostructured composites under heavy impact loading, incorporating different material combinations that are coupled in various arrangements, at different length scales, arranged in a hierarchical pattern. The material combinations feature divergent characteristics such as hard-soft or brittle-ductile, since mixture of materials with disparate properties are often found in Nature’s toughest and mechanically most robust materials, used to provide protective surfaces (e.g. in seashells, bone, spider silk). We demonstrated the development and application of such material design paradigms in studies of bone, silk, collagen (and similar materials), enabled through the development of multiscale models. Our work has pushed the frontier of biomechanics and biomaterials modeling to enable a bottom-up perspective of key issues that define robustness, strength and adaptability of biological and biologically inspired mechanically relevant materials for numerous applications.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)


A. Nova, S, Keten, N. Pugno, A. Redaelli, M.J. Buehler, “Molecular and nanostructural mechanisms of deformation, strength and toughness of spider silk fibrils”, Nano Letters, accepted for publication, DOI: 10.1021/nl101341w, 2010

Number of Papers published in peer-reviewed journals: 14.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

M.J. Buehler, “Multiscale science of biological protein materials”, Conference on Computational Physics 2010 (CCP2010), Norwegian University of Science and Technology, June 23-26, 2010 (plenary lecture)


May 20-21, 2010, “Multiscale protein material mechanics in physiologically extreme conditions and disease,” Department of Nanomedicine and Biomedical Engineering (nBME), The University of Texas Health Science Center


M.J. Buehler, “Materiomics: Deformation and failure of biological materials in extreme conditions and disease,” Brown University, Providence, RI, November 23, 2009


Number of Presentations: 10.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):


Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 1

(d) Manuscripts

D. Sen, M.J. Buehler, “Atomistically-informed mesoscale model of the mechanics of hierarchical silica composite structures from the nano- to micro-scale”, in submission


Number of Manuscripts: 3.00
## Graduate Students

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## Names of Under Graduate students supported

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**Student Metrics**

This section only applies to graduating undergraduates supported by this agreement in this reporting period:

- The number of undergraduates funded by this agreement who graduated during this period: ...... 0.00
- The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields: ...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields: ...... 0.00
- Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): ...... 0.00
- Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering: ...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense: ...... 0.00
- The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: ...... 0.00

**Names of Personnel receiving masters degrees**

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**Names of personnel receiving PHDs**

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**Names of other research staff**

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**Sub Contractors (DD882)**

**Inventions (DD882)**
Differential multi-scale modeling of chemically complex materials under heavy deformation: Biological, bioinspired and synthetic hierarchical materials

ARO Proposal # 50489-EG
Project Summary Sheets for the ARO FINAL REPORT
June 30, 2010

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This research project is focused on the analysis, modeling and design of impact mitigating coatings and thin films, utilizing nanoscale patterning and hierarchical biomimetic concepts. The goal is to create heterogeneous, hierarchical design suggestions for thin coatings capable of providing enhanced ability to mitigate high rate impact and deformation. The key new element: Use of atomistic based multi-scale modeling to explore the opportunities and potential of including the atomistic, molecular and mesoscale structure in the engineering design space by an integrated treatment of structure and material (M.J. Buehler and Y. Yung, Nature Materials, 2009; M.J. Buehler and T. Ackbarow, Materials Today, 2007; Ackbarow et al., PNAS, 2007).

The potential of a structure to mitigate impact is characterized by (i) the ability of the material to dissipate energy under high rate deformation, (ii) the resistance to brittle fracture by crack formation under high rates, and (iii) the ability to redistribute load underneath a thin external coating film.

To investigate these properties, our efforts are centered on the development of a holistic atomistic based core model of the deformation and fracture mechanisms of thin nanostructured coatings. Using atomistic simulation, we study the behavior of nanostructured composites under heavy impact loading, incorporating different material combinations that are coupled in various arrangements, at different length scales, arranged in a hierarchical pattern. This insight is then used to develop design suggestions for new nanocomposite structures.
Biological materials are adaptable, mutable...

M.J. Buehler, MIT

New blood vessels form under cyclic strain to repair wounds, provide nutrients where needed

Biological systems universally feature active components; e.g., bone remodels according to changes in loading, cells change their shape under different environments or stress

Mechanisms: Sensing of environmental cues followed by gene regulation/activation, which changes the hierarchical structure of materials ("mutability")


Challenge: Time-scales on the order of minutes, hours, days
Differential multi-scale modeling of chemically complex materials under heavy deformation

- **Objective**
  - Develop nanostructured material that resists fracture (cracking) and redistributes impact energy into plastic dissipation over large volumes

- **Approach**
  - Atomistic based, bottom-up multi-scale simulation combined with theoretical modeling, to quantify the role of length-scales and material hierarchies

- **Uniqueness of approach**
  - Our approach extends current state of the art (phenomenological models/approaches) by providing a fundamental description of material behavior under impact (cracking, plasticity, shear)
  - Provides opportunity to design material from bottom up

This slide summarizes the objective, approach and uniqueness of the approach.
Slide shows overview over multi-scale simulation paradigm. The integration of several numericals that operate at distinct length- and time-scales enables us to traverse from fundamental chemical scales (atom-atom interactions) to larger scales that are relevant for applications (that is, for measurement of material performance).
The structure of biological materials such as nacre, bone and their hierarchical organization leads to:

- a) not following the usual banana-curve for synthetic materials of strength vs toughness when we compare materials with maximal toughness and maximal strength,
- b) not following rule-of-mixtures for composite materials, and
- c) incorporating best properties of constituent materials.

For engineering materials, shown in the left figure:

1 - Conventional engineering materials (e.g. ductile metals) are tough but lack strength
2 - Conventional strong engineering materials (e.g. ceramics) show high strength but lack toughness
3 - Hierarchical nanostructured materials enable to reach high strength and high toughness (illustrates the potential of utilizing nanostructures and hierarchies)
Summary of basic approach in designing materials with multiple hierarchy to optimize strength and toughness.
This slides summarizes results obtained by our Hierarchical Bell Model, showing that hierarchies are a material **design strategy to combine disparate properties** (here strength and robustness) and thereby overcome the limitations of many engineering materials.

This first study combined only **8 elements**, which we arranged in all possible hierarchical combinations (published in Nanotechnology, 2009). This result shows that by solely changing the arrangement of alpha-helical proteins, one can control the strength-robustness performance of materials.
We then extended the study to include **32 elements**, which we arranged in all possible hierarchical combinations (published in IJAM, 2009; inaugural issue and cover paper). The results confirmed our earlier findings, and shows an even more pronounced “inverse behavior” – suggesting that by arranging the alpha-helical building blocks into hierarchies, a significant performance increase can be achieved.

The “Banana curve” (seen in conventional synthetic materials) is indicated in the plot as well.
For more than 10,000 elements (also reported in the IJAM paper), a very interesting result is obtained. First, the banana curve behavior is recovered. Second, a subset of all geometries shows the inverse banana curve behavior. Interestingly, only 2% of all structures give the inverse behavior. This means that most random arrangements of structures would lead to the banana curve behavior.

This result is important since it suggests that it is crucial to control the specific nanoscale arrangements of building blocks in order to reach high material performance.
Summary of the **interplay of size effects and hierarchical structures**. The combination of size effects and hierarchies is crucial to achieve macroscopic superior performance to combine strength and robustness.
Is structural optimization at multiple length scales (=hierarchies) the key to combine disparate material properties?

This slide illustrates how biological materials overcome the limitation of the “banana curve”. A possible explanation may be the existence of material hierarchies. Our model (previous slide) illustrates this effect at a fundamental, atomistic and molecular level.
Slides shows the next step, the **transfer of the results** obtained from studying biological protein materials towards the **design of metallic nanocomposites**. The lower part of the slide displays our model system consisting of a ductile matrix and a stiff inclusion, arranged here in a bone-like geometry.
The development of design tools for materials with multiple levels of hierarchical assembly. From the fully atomistic study of mechanics of bone-inspired nanocomposites, we obtained strength of the material as a function of shape and size and arrangement of the composite phases. The next step is to use these nanocomposites as building blocks for a second level of hierarchy. The aim is to create multi-hierarchy composites that can improve properties such as strength and toughness simultaneously through the use of design at several length scales. The figure presents an overall multi-scale approach with two levels of discretization to solve this problem. A coarse-grained method is used for the second hierarchy level. The integrated use of atomistic and coarse-grained methods will enable us to explore the broad range of structural scales relevant to initiate a new paradigm in multi-scale structural engineering.
We begin our investigation with the analysis of a single hierarchy material – representing a combination of a soft and stiff phase, forming a hetero-nanostructured composite. This is the first step to transfer the insight from biological materials to the design of bioinspired composites.

**Goal of this study:** Can we tune the large-deformation mechanical properties, and if yes, how?

The first important contribution of this work is the development of a model system that enables us to elucidate the effect of nanostructural arrangements (geometry, size, spacing, ...) on the large-deformation and impact loading properties. Based on full-atomic simulations and a multi-scale integration, we have then identified a set of important design parameters, including (i) design at the nano-level (nanocomposite), (ii) arrangement of design elements in hierarchies, (iii) interfacial properties and (iv) environmental effects on interfacial properties. These parameters represent critical factors for biomimetic design of impact resistant structures.

For example, the atomistic simulations reveal which shape, size, spacing of second phase platelets produces the maximum strength, and what changes in deformation mechanisms are seen across these geometric changes. A representative set of results will be reviewed in the next few slides.

The main finding of this large-scale atomistic simulation study is that there exists an optimal size of the platelet inclusions that leads to maximum flow stress (N. Broedling et al., *J. Mech. Phys. Solids*, 2007; D. Sen, Acta Mat., submitted). The result is significant in two ways: (i), it shows that we can indeed tune the large-deformation mechanical properties and optimize dissipation by tailoring the nanostructure, and (ii), it shows that there exists an optimal length scale at which the flow stress and thus dissipation reach a maximum. For applications, this result tells us the optimal particle size that should be dispersed in a soft matrix materials (for the example of Ni-Al the optimal size is approximately 40 nm).

We have further discovered the critical geometric parameters for maximum yield stress at large deformation (D. Sen and M.J. Buehler, Acta Mat., submitted). The studies revealed mechanistic insight into the nanoscopic stress distribution and its relation to the toughening mechanism. This result is significant since it reveals that not only the size, but also the details of the platelet arrangement is significant.

For little to no platelet offset, there is no significant strengthening effect. For platelet offset larger than 0.25 the maximum effect reaches a plateau value.

These results will guide laboratory processing techniques.
We have developed and tested a **mesoscale coarse-grained model** (similar to a finite difference method), which provides a bridge from atomistic to continuum length-scales. We are currently testing the performance of a variety of microstructural arrangements, where each phase shown here consists itself of a specific nanostructure (see previous slides). This provides a seamless integration from atomistic to continuum and the **tool could be very useful for design applications**.
The details of the constitutive law for the coarse-grained system derived from fully-atomistic simulations. This force law is used for the coupling between scales of the two hierarchy levels. (a) shows the typical bulk uniaxial stress-strain behavior for a metallic nanocomposite structure, from which elastic modulus and flow stress can be derived; (b) shows a model being fit to this loading behavior, the proportionality constants (in the inset equations) depend on lattice structure for the particle model, and are derived using the Cauchy-Born rule; (c) shows a potential application of the mesoscale model in a 2-phase 2-hierarchy material with a surface crack and material microstructural variation around it.
The particular metallic nanocomposites chosen for the 2nd hierarchy level composite. We use a soft and hard phase at 2nd H level with same stiffness but a 10 times difference of yield strength. This can be achieved by staggering platelets at the 1st hierarchy (nanocomposite) level.
The first mesoscale structure we study is a laminated composite. Laminated composites are found in protective skeletal structures in several biological systems such as sea sponges, corals. The laminated design in these materials is critical for imparting damage tolerance to the overall structure (Seshadri et al., 2002; Chai and Lawn, 2002). Our aim is similar, to maximize fracture toughness to surface cracks while minimize their plastic deformation in the interior of the materia.
Preliminary results of the laminated 2-hierarchy composite. A surface crack is created under remote mode I loading. The volume fraction of the softer phase is 0.2 and constant in all systems, but the spacing ratio between layers is varied. The red region indicates all material that has yielded at a particular loading. The effect of reducing the spacing between soft layers lead to a more spread-out plastic zones, with less penetration of the plastic zone in the interior of the material.
Material choices for bone-inspired nanocomposite structures

- Soft metal (Al, Cu) matrix – hard metal platelets (W)
- Soft metal (Al, Cu) matrix – ceramic platelets (Al₂O₃)
- Polymer matrix (PMMA/polystyrene) – CNT/graphene platelets

Polystyrene-graphene nanocomposites of different volume fractions¹

New concept: Graphene mechanics in extreme conditions
Persistent wrinkled nature of the functionalized graphene sheets within the composite provides for better interaction with the host polymer matrix. Lower figure shows fracture surface topography.
The strength of graphene-polymer interfaces is crucial to the overall load-carrying and failure mechanisms of the composite. At the interface between PMMA and graphene, a significant failure mode may be tearing of the graphene sheets from the interface. Here we look at the influence of the adhesion strength on the tearing mechanics. Figure on the left shows fragments of graphene torn from larger graphene sheets, showing a tapering behavior. On the right is the design of the computational experiment to study this behavior using molecular dynamics.
The torn sheet is seen to taper off at all adhesion strengths. We have measured the angle of taper as a function of strength of adhesion. (a) shows plot of sine of the angle of tear vs square root of the adhesion energy; (b) shows predicted angle of tear for graphene adhesion on graphite as a function of number of sheets torn off together.
Shows the atomic level virial stresses for the graphene sheet (a) and (b) show the out-of-pane shear stress \( \sigma_{gZ} \) for weak and strong adhesion strengths of 2.4 and 20.2 J/m² respectively; (c) and (d) show the in-plane tensile stress in Y direction \( \sigma_{gY} \) for weak and strong adhesion strengths of 2.4 and 20.2 J/m² respectively. Larger adhesion strengths lead to much larger tensile stresses in the sheet ahead of the crack bend. Reduction in width of the tear leads to relieving of this tensile stress, and thus the cracks tapers sharply at higher strengths. After the onset of plastic deformation, load-transfer at the polymer-graphene interface in the composite would require larger contact area, and a weaker interface is seen to increase the size of the tears, thus leading to larger load transfer.
New concept: Biomimetic silicon

How to “transform” a brittle material (here as model selected silicon) into a ductile material...
Overview of natural biological system, which shows the nanostructural arrangement of a brittle material (silica).

Can we interpret this design and use it for the design of new composites?
Structural hierarchies in two different silica-based skeletal assemblies in a marine diatom species (a-d) and a sea sponge (e-h). The diatom in (a) *Concinodicus sp.* has a silica-based exoskeleton (called frustule) made up of porous parts arranged in a hierarchical fashion (a) shows the whole frustule member (external surface of the diatom), (b) shows areola pores, the internal surface of the diatom (c) shows the 2nd central porous layer, the cribrum and (d) shows the cribellum, the external porous layer. (e) shows the external cage structure of the silica-based skeletal system of *Euplectella sp.* Scale bar 5 mm (f-g) show some of the underlying hierarchical structures with (f) showing fibre-composite structure in a constituent beam consisting of many spicules, Scale bar 20 microns, (g) single spicule showing laminated silica-protein structure, Scale bar 5 microns and (h) biosilica constituent of the silica layers revealing its consolidated nanoparticle nature, Scale bar 500 nm.
We have designed a first model system.

The following studies are focused on varying the width of the bricks and testing the influence on the mechanical behavior.

- Construct bioinspired design of silicon nanostructure
- Load in tension at 1E-5 fs
- Temperature 300 K, use: ReaxFF-Lammps
Results show that the larger systems feature a stress concentration at corners; smaller systems deform homogeneously.
Results show that the smaller systems behave in a ductile fashion, and feature large deformation with >70% strain.
(a) shows the geometry of the nano-honeycomb used as building blocks for the composite structures, (b) shows a section of the triangular mesh mesoscale particle-spring model setup, (c) show stress-strain curves obtained from atomistic simulations of a nano-honeycomb structure, and for bulk silica with a crack of the same size as the pores in the nano-honeycomb. The legend shows the classification of the nano-honeycomb structure, which is shown as \((t, p_l, p_w)\) parameters for the structure, values given in Å. The bulk silica structure shows purely brittle fracture, the nano-honeycomb structure show ductile fracture. (c) shows the behavior of the mesoscale triangular mesh lattice fitted to this constitutive behavior.
Randomly distributed particle composite structures at the mesoscale. Constituents are, bulk silica (in grey/light, with a high volume fraction) and nano-honeycomb structures (in blue/dark, small volume fraction). Design conditions that enhance toughness of bulk silica by distribution of small amount of nano-honeycomb silica are being investigated here. The structure on the left shows bulk silica particles as reinforcement, whereas the right structure shows nano-honeycomb silica particles as the reinforcing phase. Structures of both types are studied for crack propagation response.
Stress-strain curves for (a) bulk-silica reinforcing composite structures, with and without presence of a pre-crack. The near-identical response shows the flaw-tolerance behavior for these structures to pre-cracks of the given size. The structures show multiple cracking throughout the material, and this is reflected in the stress-strain curve as a gradual loss of stiffness of the material as the number and size of the multiple cracks grow. (b) Stress-strain curves for nano-honeycomb reinforcing composite structures, with and without presence of a pre-crack. The varying fracture strengths clearly show an effect of the crack size. All structures fail by the growth of a single dominant crack.
Crack pathways for composite structures with nano-honeycomb structure as the matrix and brittle silica as the reinforcing particulate phase. The volume fraction of silica phase is 76%. (a) and (b) show fracture progress starting from a material with no pre-crack; (c) and (d) show fracture progress in the same material with a pre-crack present. In cases we observe that the pre-crack propagates for a small distance but does not propagate through the sample, and other smaller cracks are initiated throughout the sample. These multiple small cracks determine the stress-strain response of the structure. The structure is thus flaw-tolerant to pre-cracks of these sizes, and the fracture stress and behavior are almost independent of the size of the pre-crack. This is reflected also in the stress-strain curve for the stress-strain response of the uncracked, and cracked structures (shown in Figure 4a). A fracture toughness cannot be measured for these structures and crack sizes.
Crack pathways for composite structures with brittle silica as the matrix and nano-honeycomb structure as the reinforcing particulate phase. The volume fraction of bulk silica phase is 86%. (a) and (b) show fracture progress starting from a no pre-crack material; (c) and (d) show fracture progress from the same material with a pre-crack. In both cases we observe that fracture occurs through the propagation of a dominant crack. (a) and (d) show the un-cracked and pre-cracked specimens at the same load, the un-cracked specimen is intact, whereas the pre-crack has started propagating in the other specimen. Since the fracture strength of a structure with a dominant propagating crack is pre-crack-size dependent (according to fracture mechanics), the stress-strain curve for the stress-strain response of the undefected, and cracked structures are markedly different (shown in Figure 4b). Fracture toughness can be measured for these structures, as the energy required for the growth of the pre-crack.
Different composite structures with brittle bulk-silica as the matrix (volume fraction 86%) and ductile nano-honeycomb structures as the reinforcing particulate phase showing fracture toughness improvement mechanisms. The particles have circular cross-section and are randomly distributed and five different random structures are shown here. A single pre-crack is introduced and then subjected to mode I loading. Propagation of the single dominant crack is seen on loading, and the propagation path is marked in white. All structures show that the crack path is not straight, but connects reinforcing particles lying close to the original crack plane. Crack deflection and bridging by reinforcing particles behind the crack tip are the mechanisms seen to increase toughness here.
Left: Calculation of the J-integral and R-curves. (a) shows the J-integral calculation for a stationary crack by the use of a domain-integral around the crack. The J-integral provides the value of the energy release rate per unit advance of the crack into the crack tip, or the resistance to crack propagation. The red/dark region shown is the domain of integration and the convergence of the J-integral is tested by taking different $r_1$ and $r_2$ regions for the same crack and specimen configuration. (b) shows fracture toughness measures as a function of crack advance (R-curve behavior) for all the structures in Figure 8. The toughness of bulk silica is also shown as a dotted curve. Right: The design of the hierarchical silica composite improves the toughness of bulk silica significantly (≈5.5 times) while compromising on the stiffness only slightly (≈70% of bulk). This points towards the use of hierarchies along with a single design material to improve undesirable mechanical properties significantly (here low toughness) while not compromising on the desirable ones (here high stiffness).
Our research suggests new opportunities to meet challenges of a lighter, faster and more adaptable Army by introducing greater material complexity. Thereby, the use if hierarchies and novel material concepts as studied in our project may be critical to achieve the target properties.

As shown earlier, the merger of structure and material is believed to be a key aspect that will enable us to meet the challenges of Defense applications.
A Materiomics Approach Towards Bioinspired Intelligent and Active Armor Materials

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Talk given at: Workshop on Intelligent and Active Protective Systems for Dynamic Load Mitigation • May 27-28, 2010

Funding: ARO (Bruce LaMattina)
“Material (pie) in the sky”—what if we could…

- ... make a **diversity** of functional materials out of the **same** universal building blocks?

  *E.g. use simple chemistry, abundant materials (protein, silica)*

- ...make materials at **low energy cost**, with low weight (density), and yet superior properties (all of the above)?

  *E.g. avoid high temperature processing*

- ...make **adaptable** materials, which change properties based on need, e.g. via external stimuli (light, electric field, pH, water…)?

  *E.g. mechanical response changes dramatically based on threat type ("modes" of operation)*
Have in abundance: natural materials

sand

water & rocks

soy beans (protein)
Need: functional materials, devices, armors…

RoboTroop
The US Army’s vision for 2030. Many of these technologies are already under development.

- The headgear has biometric facial recognition to identify insurgents, while targets are illuminated on the display.
- Advanced nanomaterial armor protects against blasts, burns, and rifle rounds. The entire ensemble is embedded with behavioral and physiological sensors that continuously monitor the soldier’s health.
- The "data glove" may be used to operate robots and unmanned drones.
- The external armor, or "skeleton," not only provides the protection of traditional body armor, it enhances the strength of soldiers’ legs.
- The custom-fit boot will be designed to minimize effort and increase endurance.

Sources: US Army
Core question: *How to turn abundant materials into functional materials?*

Less energy, lighter, stronger, adaptable, easily available…

*Path to success – understand biological materials*
Biological highly functional materials – *diatoms, sea sponges, organisms*
Protein materials in biology

Eye’s cornea
(optical/mechanical, collagen material)

Skin
(protection, complex composite of collagen, elastin)

Cells
(complex material/system based on structural proteins)

Nerves
(signaling)

Blood vessels
(mass transport)

Tendon
(links bone, Muscles, “glue”, e.g. Achilles tendon, collagen)

Cartilage
(reduce friction in joints)

Bone
(structural stability, collagen/minerals)

Muscle tissue
(mechanical force, motor proteins)

Genes (DNA structure) define protein structure

ACGT

Four letter code “DNA”

Combination of 3 DNA letters equals a amino acid

E.g.: Proline –
CCT, CCC, CCA, CCG

Transcription/translation

.. - Proline - Serine -
Proline - Alanine - ..

Sequence of amino acids
“polypeptide” (1D structure)

Folding
(3D structure)

M. Buehler et al., Nature Materials, 2009
Protein material assembly

**Folded protein**

**Intermediate filaments**

**Self-assembly processes** (e.g. lamin intermediate filaments)

**Experimental analysis** (Herrmann, Aebi, Kreplak et al.)

How do fiber and larger-scale material properties (s.a. elasticity, deformability, failure, fracture, etc.) depend on the structure of the constituting protein structure?

Tendon, bone

“macroscale”
Collagenous tissues – an issue (tissue) of multiple scales

Biological materials are adaptable, mutable...

Biological systems universally feature active components; e.g.: bone remodels according to changes in loading, cells change their shape under different environments or stress.

**Mechanisms:** Sensing of environmental cues followed by gene regulation/activation, which changes the hierarchical structure of materials (“mutability”)


**Materiomics**

New blood vessels form under cyclic strain to repair wounds, provide nutrients where needed.


**Challenge:** Time-scales on the order of minutes, hours, days
Linking chemistry, structure and mechanics

**Molecular dynamics:**
Fundamental model of materials
“bottom-up”

\[ U_{\text{system}} = U_{\text{bond}} + U_{\text{angle}} + U_{\text{torsion}} + U_{\text{Coulomb}} + U_{\text{vdW}} + \ldots \]

**covalent bonds**
- bond stretching
- angle bending
- bond rotation

**electrostatic bonds**
- electrostatic interactions

**weak bonds**
- vdw interactions

Integration with experimental techniques

Functionality

Feed parameters
Finer trains coarser

Key tool:
Large-scale computing

M. Buehler et al., Nature Materials, 2009
Pulling on a single collagen molecule

Pulling on a single collagen molecule

Coarse-graining

Mechanism: Entropic elasticity (change in configurational entropy)

Advancement in experimental equipment: Have quantitatively confirmed predictions from our simulations

Sun et al., J. Biomechanics, 2004; Buehler and Wong, Biophys. J., 2007
Hierarchical features of soft collagenous tissue

B. Moran, M. Buehler et al., Annals in Biomedical Engineering, 2009
Materials failure in biology and engineering

Rapid aging disease progeria: mechanical failure of cell nucleus

Airplane crash: failure of engineering structure
Rat kangaroo kidney epithelial - immunofluorescently labeled for keratin (intermediate filament)
Vimentin intermediate filaments (IF)

Organize the internal structure of cells

Provide strength & very extensible (300%) – *source unknown, mechanisms unknown, …*

Cell

Cytoskeleton

Full length filaments

Unit-length filaments (8 tetramers)

Tetramers (2 dimers)

Dimer (elementary building blocks)

nano

macro

force

intermediate filaments

microtubules

Deformation

Janmey *et al.*

10 nm

>240 nm

>1 μm

>50 μm

0.5 μm

20
Intermediate filaments – widely found in nature

neuron cells (brain)

hair, hoof

fibroblast cells (make collagen)

cell nucleus
Intermediate filaments dimer structure

Crystallized: Part of 1A and 2B (structure not known of other parts)

$\phi = -58^\circ$

$\psi = -47^\circ$

Amino acid sequence (genetics)

Initial structural model

Energy minimization & equilibration (repeat until convergence)

Validation

Final structure

Z. Qin, L. Kreplak, M. Buehler, PLoS ONE, 2009
Structure prediction and functional properties

Genetics

...GGLGGQGAGA
AAAAAGGGAGQG...

Amino acid sequence → Replica Exchange Simulations

Validation (experimental results) → Ensemble of final structures

Mechanical characterization (multiscale)

Mechanics (functionality)
Molecular structure of the dimer and tetramer

Dimer

Linker domains provide flexible “hinges”

Tetramer

Linker L2 provides assembly template

Z. Qin, L. Kreplak, M. Buehler, Nanotechnology, 2009; PLoS ONE, 2009
Stretching of intermediate filament protein

Larger-scale protein network properties

How does behavior of protein network at larger scale depend on the protein constituent’s structure?

Kreplak et al., 2006

Aebi et al., Nature, 1984
Lamin intermediate filament network (cell nucleus)

Ackbarow et al., PNAS, 2007; Ackbarow, Buehler et al., PLoS ONE, 2009
Coarse-graining approach
Movie of deformation

Intermediate filament


Z. Qin, L. Kreplak, M. Buehler, PLoS ONE, 2009;
Z. Qin et al., unpublished
Deformation behavior of alpha-helix network under strain

Self-protecting mechanism

Ackbarow, Buehler et al., PLoS ONE, 2009
Hierarchical levels and associated mechanisms

**Structural transformation** of crack-like defects to mitigate stress concentrations

**Distance between filaments** facilitates extreme strain gradients at low energy cost

Parallel AHs & long linear array of turns provides structural basis for large extensibility via repeated rupture of turns; A-B-transition

Clusters of 3-4 H-bonds provide optimal resistance against mechanical failure (3-4 H-bonds break concurrently)

H-bonds form at moderate temperatures: Self-assembly of alpha-helices/self-healing

Ackbarow et al., PNAS, 2007; Ackbarow, Sen, Thaulow, Buehler, PLoS ONE, 2009
I will highlight a few of the disciplines in which we have elected to increase our efforts. In FY11, the Army will increase its focus on developing the scientific foundations leading to the discovery of novel materials with extraordinary performance characteristics of particular interest to the Army, such as ballistic protection. The robust research approach will emphasize multi-scale modeling and simulation for performance prediction and design of materials under extreme conditions (high strain rate, temperature, pressure, etc.). This modeling effort, supported by in-house and extramural experimental studies, will study a range of material classes (such as structural, electronic, energetic) and coupled disciplines (e.g., mechanics and electromagnetics) enabling two-way information transfer across the length scales from the molecular level up to the material system level.
Mechanical response of spider silk

1-2 GPa

Spider silk with diameter of $O$(inch) can stop large aircraft in flight

Spider silk’s hierarchical structure

**Macro**
- Spider web (macro)
- Skin
- Fibrils
- Core

**Nano**
- Beta-crystal
- Amorphous phase
- H-bonded beta-crystals
- H-bonded beta-strand
- H-bond (chemical structure)

**Beta-strand protein motif**
Scaling of strength of H-bond assemblies

Characteristic maximum number of H-bonds work cooperatively: 3-4 H-bonds

Many small segments with 3-4 HBs each enhance the strength multiple times

Intrinsic energetics, nanomechanics, and structural confinement control strength properties: Reach strength at characteristic dimension of H-bond clusters

Size effects of strength of beta-sheet proteins

Keten and Buehler, Physical Review E, 2008
Validation against experiment

Simple model explains many experiments, has implications for a wide range of polymeric materials.

Theory predicts near-equilibrium strength of beta-proteins accurately to be around 50-300 pN.

Cluster size in natural protein materials

Properties of H-bonds

H-Bond energy: 2-10 kcal/mol

Thermal energy scale

\[ k_B T \approx 0.6 \text{ kcal/mol (room temp)} \]

controls unique properties of water

Water: liquid @ 300K

Protein: solid @ 300K

WHY?

individual H-bonds in water
Hierarchical assembly – from nano to macro

- Protein filaments and protein materials constitute hierarchical assemblies, from nano to macro
- H-bonds provide a “universal glue” found in proteins (e.g. alpha-helices, beta-sheets, etc.) – **Nature’s cement**
- Fundamental question—mechanical properties of H-bonds
Universal building blocks, diverse structures (and thus, functions)

brick + cement ← universality → polypeptide + H-bond

castle → bridge → house

diversity

M. Buehler et al., Nature Materials, 2009
Mechanical response of spider silk

1-2 GPa

Spider silk’s hierarchical structure

S. Keten, M. Buehler, APL, 2010
Structure prediction and functional properties

Genetics

...GGLGGQGAGA
AAAAAGGAGGQG

Amino acid sequence

Replica Exchange Simulations

Validation (experimental results)

Ensemble of final structures

Mechanical characterization (multiscale)

Mechanics (functionality)
Replica Exchange approach (parallelized)

Simulate copies of same system with different temperatures
Exchange configurations between them
Evaluate most stable configurations obtained at low temperature = solution “ensemble” of structures

S. Keten, M. Buehler, APL, 2010
Search for most likely conformations

**Key finding:** Secondary structure is dominated by beta-sheets (mostly seen in poly-Ala regions), as well as turn type structures. This is in line with what has been observed in spider silk. (% below show relative amount of respective secondary structure)

- **HELIX:** 0%
- **BS** : 49.78%
- **COIL** : 19.56%
- **TURN** : 30.67%

- **HELIX:** 0.78%
- **BS** : 47.44%
- **COIL** : 15.89%
- **TURN** : 35.89%

- **HELIX:** 0.44%
- **BS** : 40.44%
- **COIL** : 15.67%
- **TURN** : 43.44%

S. Keten, M. Buehler, *APL*, 2010
Experimental validation

- poly-Ala regions form beta-sheet regions with stacking to accommodate methyl side-chains. These interlocked regions are densely packed and orderly.

- Glycine residues predominantly lie in the $3_1$ helix structural conformation, with occasional type II beta-turn structures. $3_1$ helix structure is supported by CA(i)-CA(i+3) distances, being most probable around 9 Å, as well as existence of interchain H-bonds. Packing of chains is disorderly.

S. Keten, M. Buehler, *APL*, 2010
Detailed view of structure

3\_1 helix

S. Keten, M. Buehler, *APL*, 2010
Mechanical analysis of spider silk

- Apply force to half of the strands in each direction (7 total). Strands are randomly selected to mimic loading conditions in spider silk.
- A constant force is applied to each strand and systems is equilibrated. Loading rate (pN/time) is kept constant for each addition of force [here 0.2 pN/ps]
- Extension is taken from the center of mass of pulled atoms, converted to strain based on initial distance.
- Cross sectional area taken as 4 nm² for all systems

S. Keten, M. Buehler, APL, 2010
Force-deformation behavior

- slip & breaking of beta-crystals
- loss of turn structure
- yielding

S. Keten, M. Buehler, J. Roy. Soc. Interface, 2010
Deformation analysis of spider silk

Spider silk’s hierarchical structure

Macro:
- Spider web (macro)
  - Skin
  - Fibrils
  - Core

Nano:
- Beta-crystal
  - H-bonded beta-crystals
  - H-bond (chemical structure)
  - Amorphous phase

Beta-crystal (key for cross-linking)

Size effects in silk nanocrystals

pull-out setup (small system)

pull-out setup (large system)

stick-slip mechanism

crack formation & propagation

Size effects in silk nanocrystals

Size effects in silk nanocrystals

$s = \text{ratio of shear vs. bending contributions to displacement}$

$L^*$ for $s=1$

$s(L) = \frac{3D_B}{L^2D_T} = \frac{1}{4} \frac{Eh^2}{GL^2} \sim \frac{h^2}{L^2}$

Interplay of scaling laws in spider silk

*Kelen, Xu, Ihle, Buehler, Nature Materials, 2010*

Natural silk: $L^* = 2-7$ nm and $h^* = 2-3$ nm
Larger-scale model of silk (1000 nm)

How do nanoscale structures & properties define larger-scale mechanical properties?

Keten, Nova, Buehler et al., *Nano Letters*, 2010
Nova et al., in preparation
Molecular model explains experimental results: Size effect a direct result of structural changes with profound impact on macroscale mechanical behavior.

Merger of structure and material

Universality and diversity (universality-diversity paradigm)

Create multifunctionality (diversity) by changing structural arrangements of few (universal) constituents rather than inventing new building blocks.

M. Buehler, Nature Nanotechnology, 2010
Concept – mutable materials

Concept: Change structure of material at defined scales
Thereby: Induce change in mechanical, optical, thermal etc. properties

NSF-IRG
with C. Ortiz et al.

M. Buehler, Nature Nanotechnology, 2010
Practical impact: Transfer to synthetic fiber design based on nanomaterials

MURI 2009-2014 (ARO PM D. Stepp, D. Kiserow)
PI: H. Espinosa (NWU), with M. Buehler (MIT) et al.

Results presented at MURI Kickoff Meeting, March 1 2010, Aberdeen, MD
Wood-inspired CNT bundles
Inspired by biological structures (e.g. cell, left), controlled assembly of nanostructures into functional materials (e.g. by using hierarchies), some of the challenges can be addressed.

Xu and Buehler, *Nano Letters*, 2009
diatoms (silicified algae)
Hierarchical structure of sea sponges, diatoms

Hierarchical structure of diatoms, showing their porous silica structure

Garcia and Buehler, COMMAT, 2010

Losic et al. Advanced Materials, 2009

AFM and SEM images of various diatom species
Silica and silicon is abundant, **but brittle**

Silicon and oxygen – most abundant material in earth’s crust

But – not useful as material (brittle)

Sen, Buehler, et al., PRL, 2010
Diatoms – Nature’s flexible armor

Garcia and Buehler, COMMAT, 2010

Model system to probe effects of nonporous structure on material performance

Controlled parameter width $w$
Mechanism of deformation

“small” – continuous shape change, ductility

“large” – cracking

Garcia and Buehler, COMMAT, 2010
An opportunity for the future

Tank & armor out of glass & soy bean?
Abundant, cheap (low energy), stores CO$_2$ (diatoms)…
Big computers allow for atomistic simulation: New paradigm of studying protein materials – “bottom-up” approach

Protein materials must be understood at multiple scales – from the level of individual proteins, to fibrils, fibers, tissues, etc.

Mechanical properties matter in biology - understanding failure is the key to success:
- Source of strength, robustness, adaptability (remodeling)
- Mechanisms in diseases and injuries (genetic diseases, cancer, etc.)
- Transfer to bioinspired designs (engineering)