REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. REPORT DATE (DD-MM-YYYY)	2. REPORT TYPE	3. DATES COVERED (From - To)
29-06-2010	Final Report	1-Aug-2006 - 30-Jun-2010

4. TITLE AND SUBTITLE
Differential multiscale modeling of chemically complex materials under heavy deformation: Biological, bioinspired and synthetic hierarchical materials

5a. CONTRACT NUMBER
W911NF-06-1-0291

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
611102

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

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7. PERFORMING ORGANIZATION NAMES AND ADDRESSES
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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSOR/MONITOR'S ACRONYM(S)
ARO

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
50489-EG.37

12. DISTRIBUTION AVAILABILITY STATEMENT
Approved for Public Release; Distribution Unlimited

13. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. 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

15. SUBJECT TERMS
Materials failure, molecular dynamics simulation, fracture, plasticity, nanomaterial, hierarchical structures, chemical complexity, strength, energy dissipation

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			Markus Buehler
UU	UU	UU	UU		19b. TELEPHONE NUMBER 617-452-2750

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

Report Title

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

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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)

D. Sen, C. Thaulow, S. Schieffer, A. Cohen, M.J. Buehler, “Atomistic study of crack-tip cleavage to dislocation emission transition in silicon single crystals”, Physical Review Letters, Vol. 105, paper # 235502, 2010.

M.J. Buehler, Z. Xu, “Mind the helical crack”, Nature, Vol. 464(4), pp. 42-43, 2010

A.P. Garcia, M.J. Buehler, “Bioinspired silicon nanoporous bulk material provides great toughness at great deformability”, Computational Materials Science, Vol. 48(2), pp. 303-309, 2010

S. Keten, Z. Xu, B. Ihle, M.J. Buehler, “Nanoconfinement controls stiffness, strength and mechanical toughness of beta-sheet crystals in silk”, Nature Materials, Vol. 9, pp. 359-367, 2010.

Z. Xu, M.J. Buehler, “Hierarchical assemblies of graphene nanoribbons through hydrogen bonds”, Nanotechnology, Vol. 20(37), paper # 375704, 2009; Highlighted in: Nanotechweb Lab Talk, “Scaling up graphene nanoribbons – a bioinspired solution” (Sept. 23, 2009) http://nanotechweb.org/cws/article/lab/40458

S. Cranford, D. Sen, M.J. Buehler, “Meso-Origami: Folding Multilayer Graphene Sheets”, Applied Physics Letters, Vol. 95, paper #: 123121, 2009

D. Sen and M.J. Buehler, “Size and geometry effects on flow stress in bioinspired de novo metal-matrix nanocomposites”, Advanced Engineering Materials, Vol. 11(10), pp. 774-781, 2009

M.J. Buehler, “Strength in numbers”, Nature Nanotechnology, Vol. 5, pp. 172-174, 2010

M.J. Buehler, S. Keten, “Failure of molecules, bones, and the earth itself”, Rev. Mod. Phys., Vol. 82(2), 2010

R. Jack, D. Sen, M.J. Buehler, “Graphene nanocutting through nanopatterned vacancy defects”, Journal of Computational and Theoretical Nanoscience, Vol. 7, pp. 354-359, 2010.

M.J. Buehler, Y.C. Yung, “How protein materials balance strength, robustness and adaptability”, HFSP Journal, Vol. 4(1), pp. 26-40, 2010

M.E. Launey, M.J. Buehler, R.O. Ritchie, “On the mechanistic origins of toughness in bone”, Annual Review of Materials Science, accepted for publication

D. Sen, K. Novoselov, P. Reis and M.J. Buehler, “Tearing of graphene sheets from adhesive substrates produces tapered nanoribbons”, Small, available online: DOI 10.1002/smll.201000097, 2010

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, Z. Qin, L. Kreplak, “In Silico Structure Prediction and Nanomechanics of Intermediate Filaments”,16th US National Congress of Theoretical and Applied Mechanics, State College, PA, June 27 - July 2, 2010 (keynote)

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 lecutre)

M.J. Buehler, “In silico structure and nanomechanics of intermediate filaments”, Gordon conference on Intermediate Filaments, Tilton School, Tilton, NH, June 20-25, 2010

M.J. Buehler, “Multiscale failure mechanics of hierarchical biological protein materials”, E-MRS Spring Meeting 2010,Strasbourg, France, June 7-11, 2010

May 30-June 4, 2010, “Materiomics: Multiscale Science of Hierarchical Biological Materials, from Nano to Macro,” EUPOC 2010, Hierarchically Structured Polymers, Gargnano Lago di Garda, Italy.

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

May 23-26, 2010, “Multiscale science of protein materials in extreme conditions and disease,” SIAM Conference on Mathematical Aspects of Materials Science, Philadelphia, PA.

M.J. Buehler, “Deformation and failure of biological materials in extreme conditions,” Workshop on: Modeling Biological Materials: Soft Tissue and Biologically Inspired Materials, Institute for Applied Mathematics and Computational Science (IAMCS), Texas A&M University, Jan. 27-28, 2010

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

M.J. Buehler, “Deformation and failure of biological materials in extreme conditions and disease,” Squishy Physics & Pizza Seminar Series, School of Engineering and Applied Science, Harvard University, Cambridge, MA, December 2, 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):

D. Sen, A. Thompson, A. Van Duin, W.A. Goddard, M.J. Buehler, “Direct atomistic simulation of brittle-to-ductile transition in silicon single crystals”, Symposium on Amorphous and Polycrystalline Thin-Film Silicon Science and Technology, MRS Spring Meeting, San Francisco, CA, Volume 1245, 2010

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

D. Sen, A. Garcia, M.J. Buehler, “Mechanics of nano-honeycomb silica structures: A size-dependent brittle-to-ductile transition”, Journal of Nanomechanics and Micromechanics, in submission

A. Garcia, D. Sen, M.J. Buehler, “Hierarchical silica nanostructures inspired by diatom algae yield superior deformability, toughness and strength”, Metallurgical and Materials Transactions A, in submission

Number of Manuscripts: 3.00

Patents Submitted

Patents Awarded

Graduate Students

NAME	PERCENT_SUPPORTED
Dipanjan Sen	1.00
Zhao Qin	0.00
Sinan Keten	0.00
Andre Garcia	0.00
FTE Equivalent:	**1.00**
Total Number:	**4**

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Markus J. Buehler	0.08	No
FTE Equivalent:	**0.08**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
Britni Ihle	
FTE Equivalent:	
Total Number:	**1**

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

NAME

Total Number:

Names of personnel receiving PHDs

NAME
Sinan Keten

Total Number: 1

Names of other research staff

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Sub Contractors (DD882)

Inventions (DD882)

M.J. Buehler, MIT

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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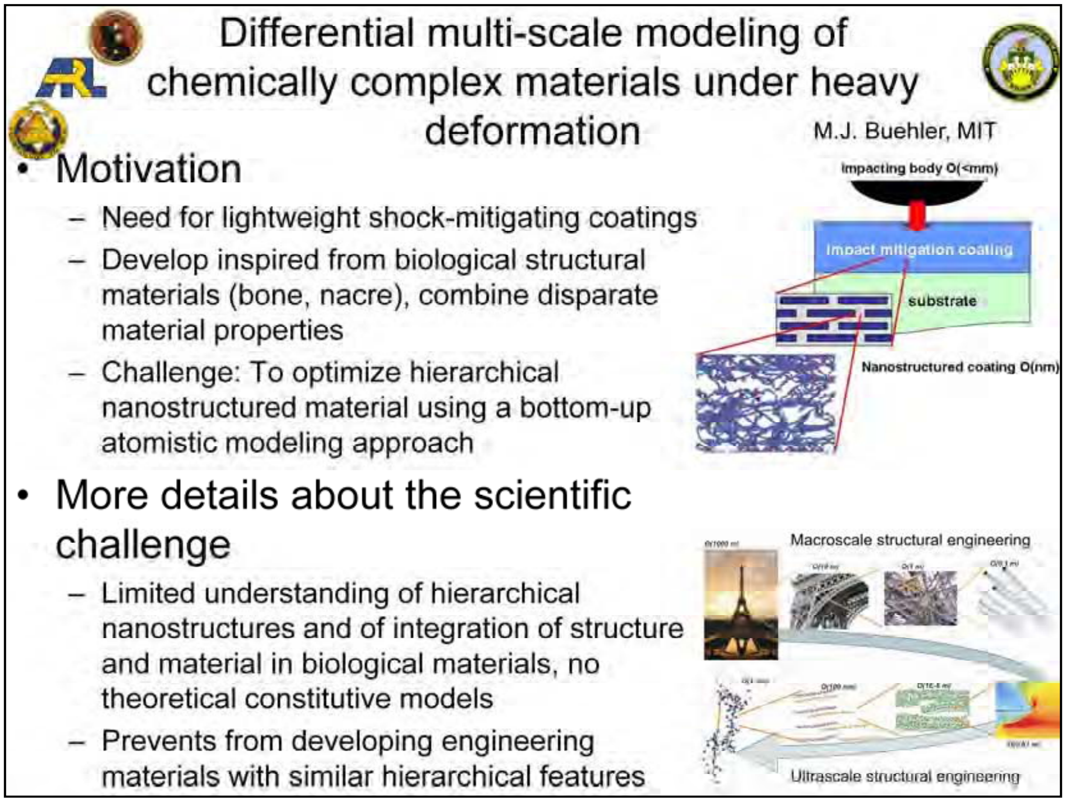


This research project is focused on the analysis, modeling and design of impact mitigating coatings and thin films, utilizing nanoscale patterning and hierarchical biomimetic concepts. The goal is to create heterogeneous, hierarchical design suggestions for thin coatings capable of providing enhanced 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.

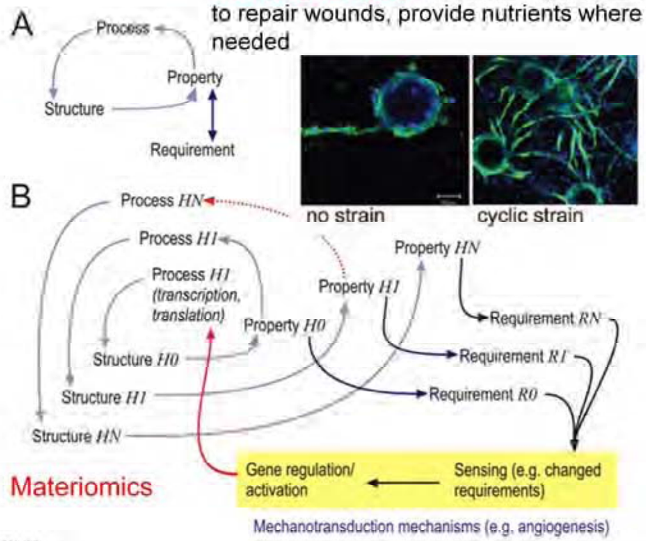
Biological materials are adaptable, mutable…

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")



Materiomics

Buehler and Yung, *Nature Materials*, 2009

Y. Yung, M. Buehler, D. Mooney, *et al.*, *PNAS,* 2009

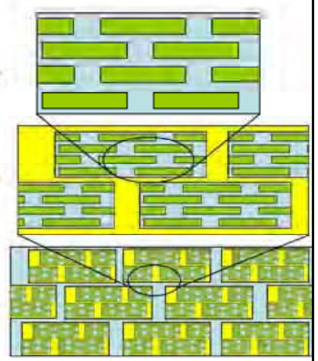
Challenge: Time-scales on the order of minutes, hours, days

3

Differential multi-scale modeling of chemically complex materials under heavy deformation

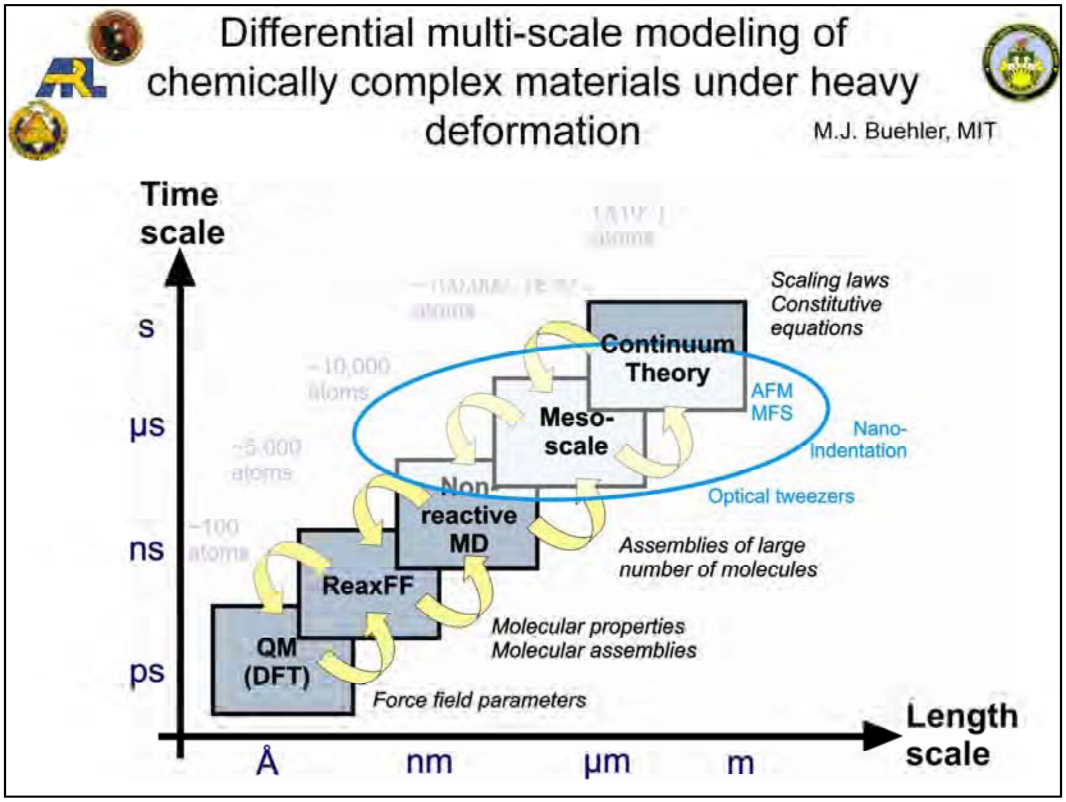
M.J. Buehler, MIT

- 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

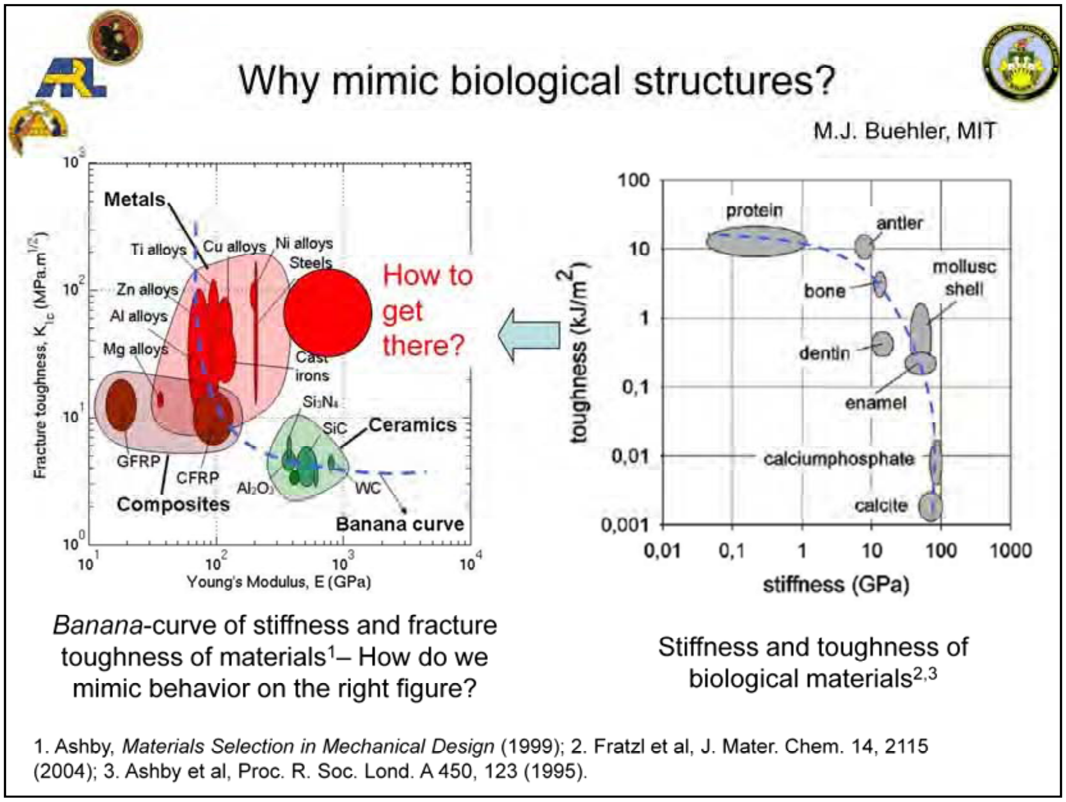


Hierarchical structures with characteristic features at multiple scales

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

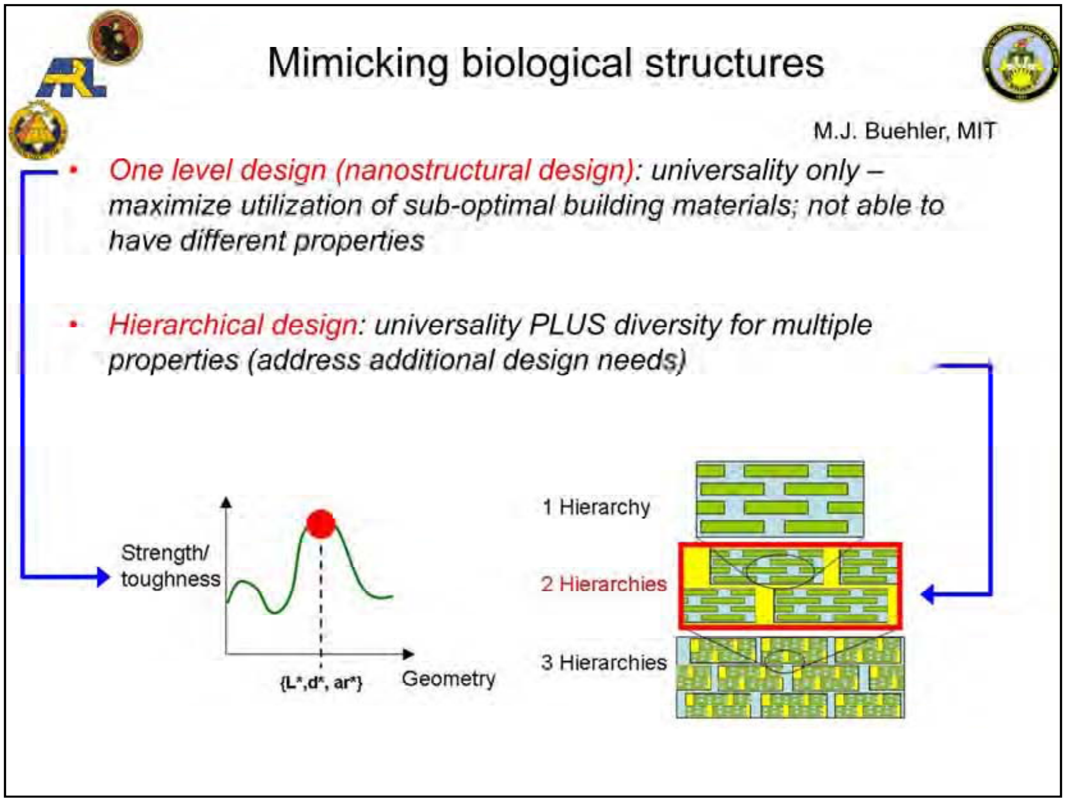
c) incorporating best properties of constituent materials.

For engineering materials, shown in the left figure:

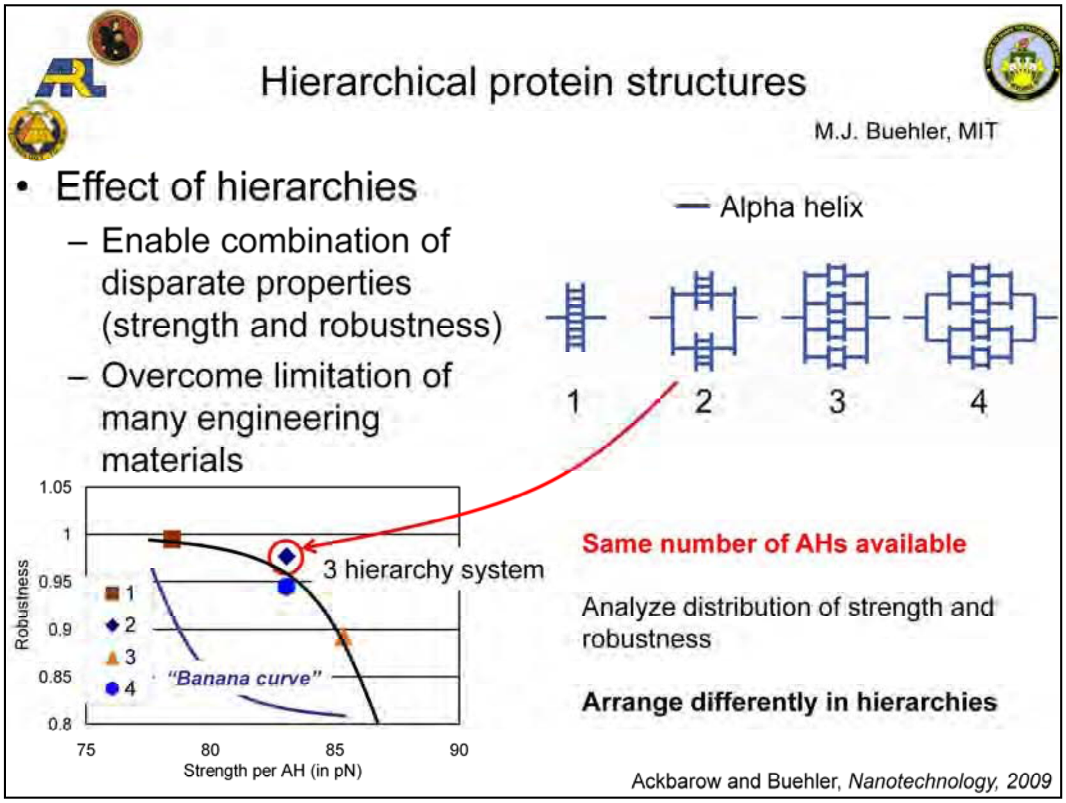
1 - Conventional engineering materials (e.g. ductile metals) are tough but lack strength

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)

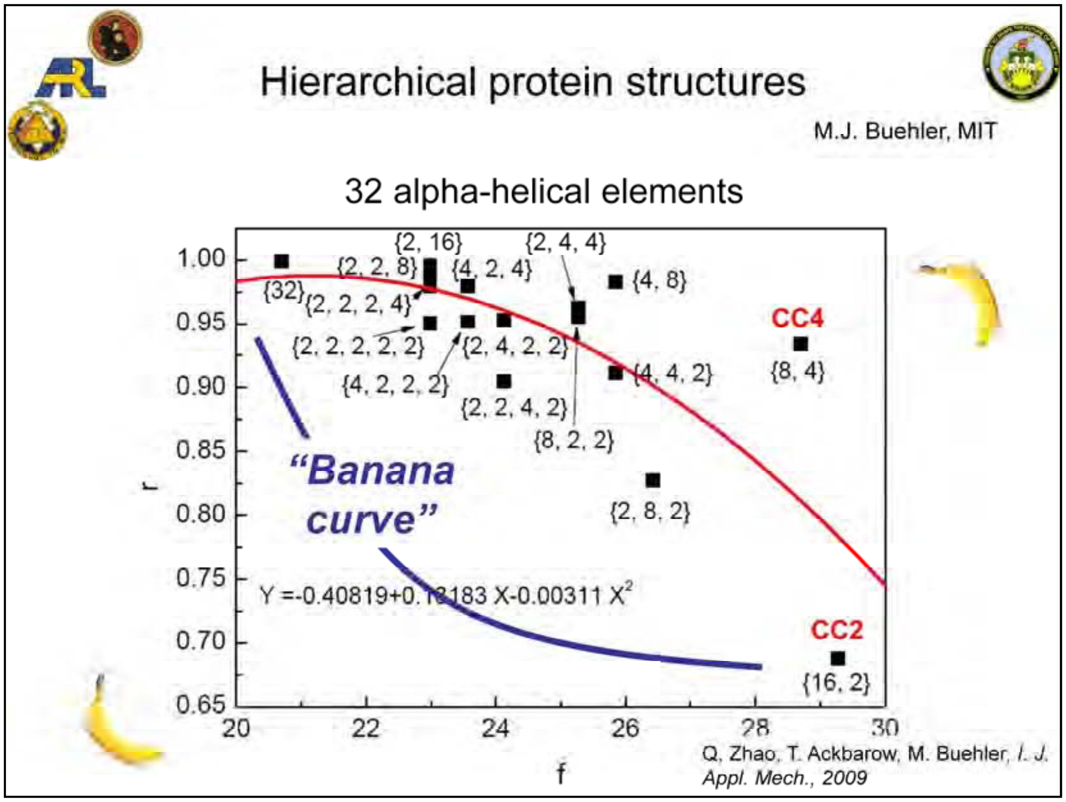


Summary of basic approach in designing materials with multiple hierarchy to optimize strength and toughness.



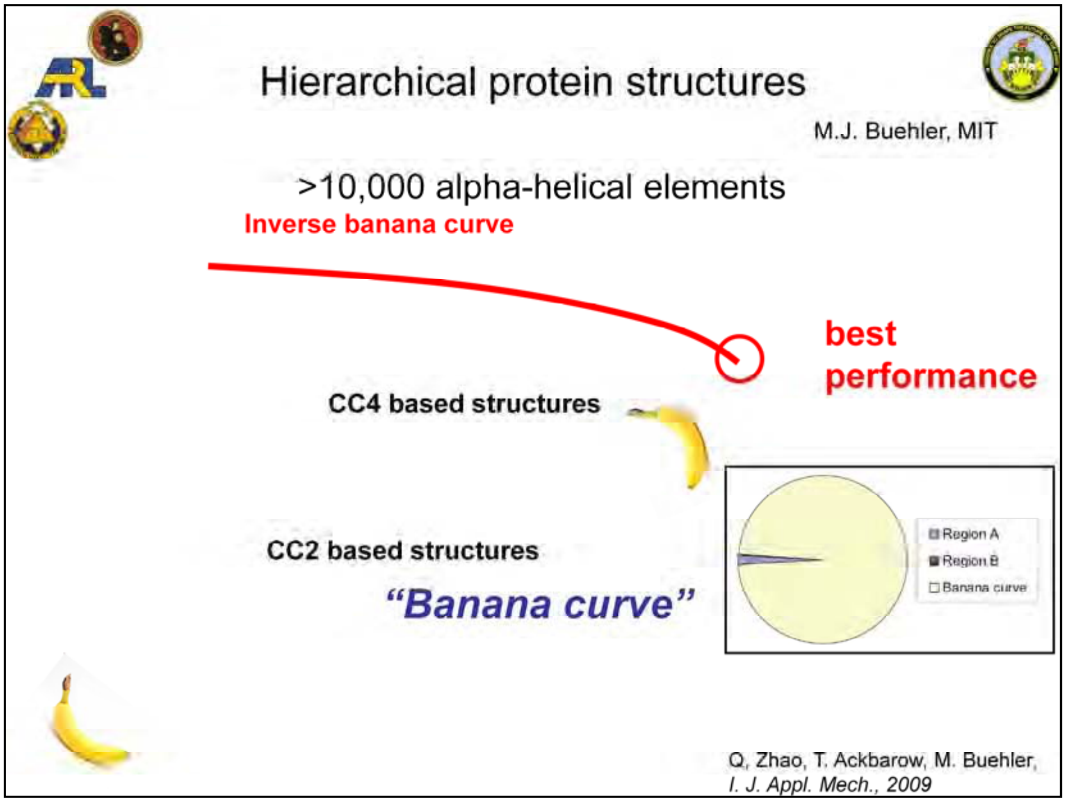
This slides summarizes results obtained by our Hierarchical Bell Model, showing that hierarchies are a material **design strategy to combine disparate properties** (here strength and robustness) and thereby overcome the limitations of many engineering materials.

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.



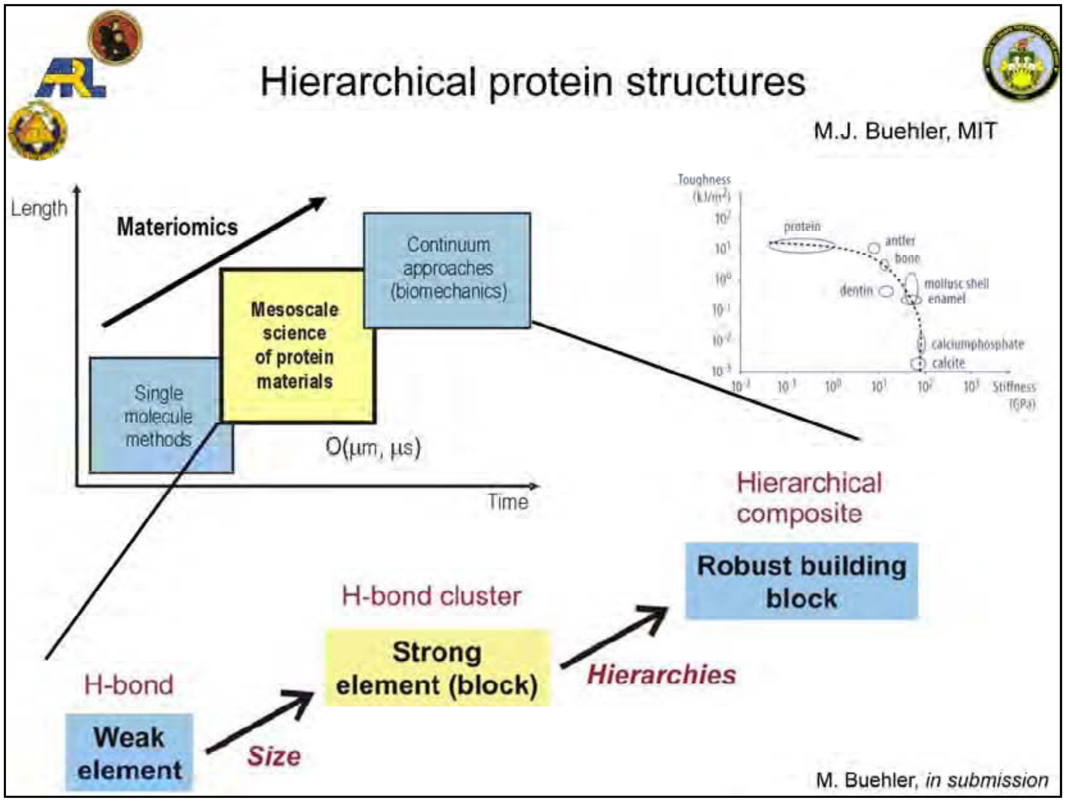
We then extended the study to include **32 elements**, which we arranged in all possible hierarchical combinations (published in IJAM, 2009; inaugural issue and cover paper). The results confirmed our earlier findings, and shows an even more pronounced "inverse behavior" – suggesting that by arranging 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.

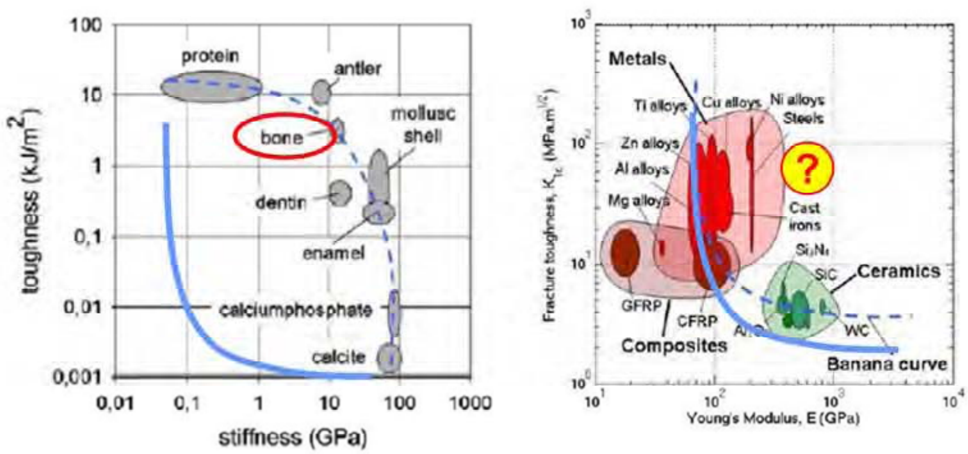
This result is important since it suggests that it is crucial to control the specific nanoscale arrangements of building blocks in order to reach high material performance.



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.

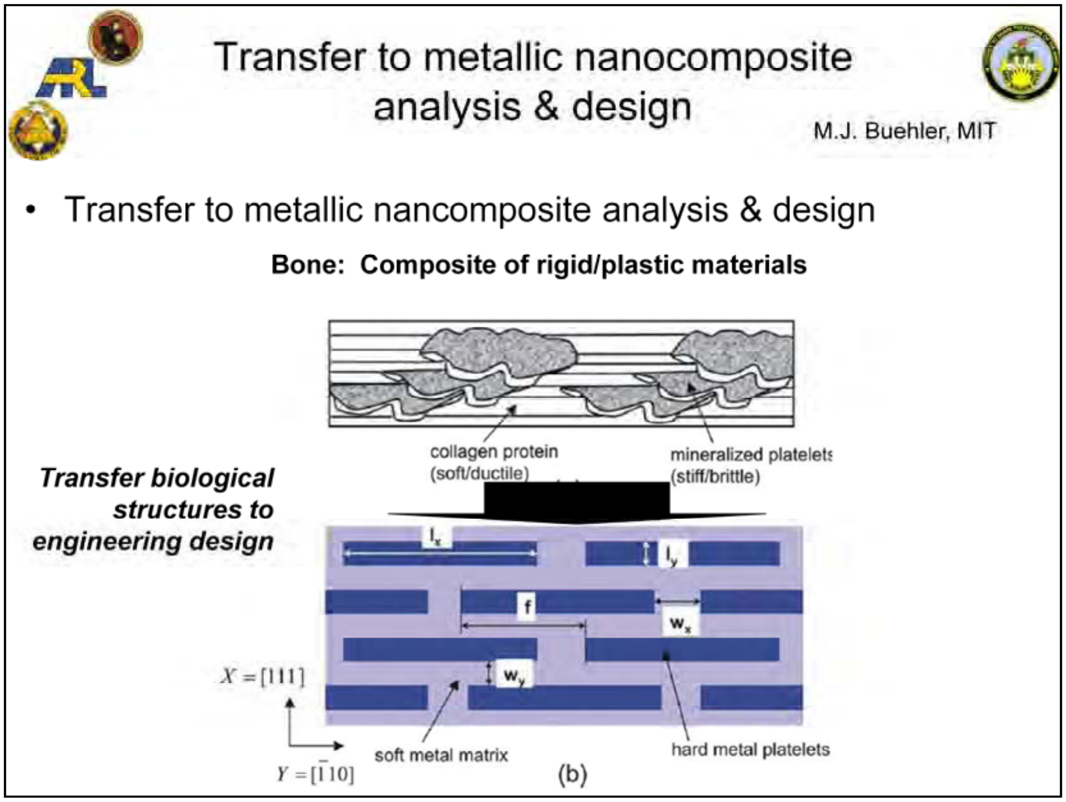
Performance of biological vs. synthetic materials

M.J. Buehler, MIT

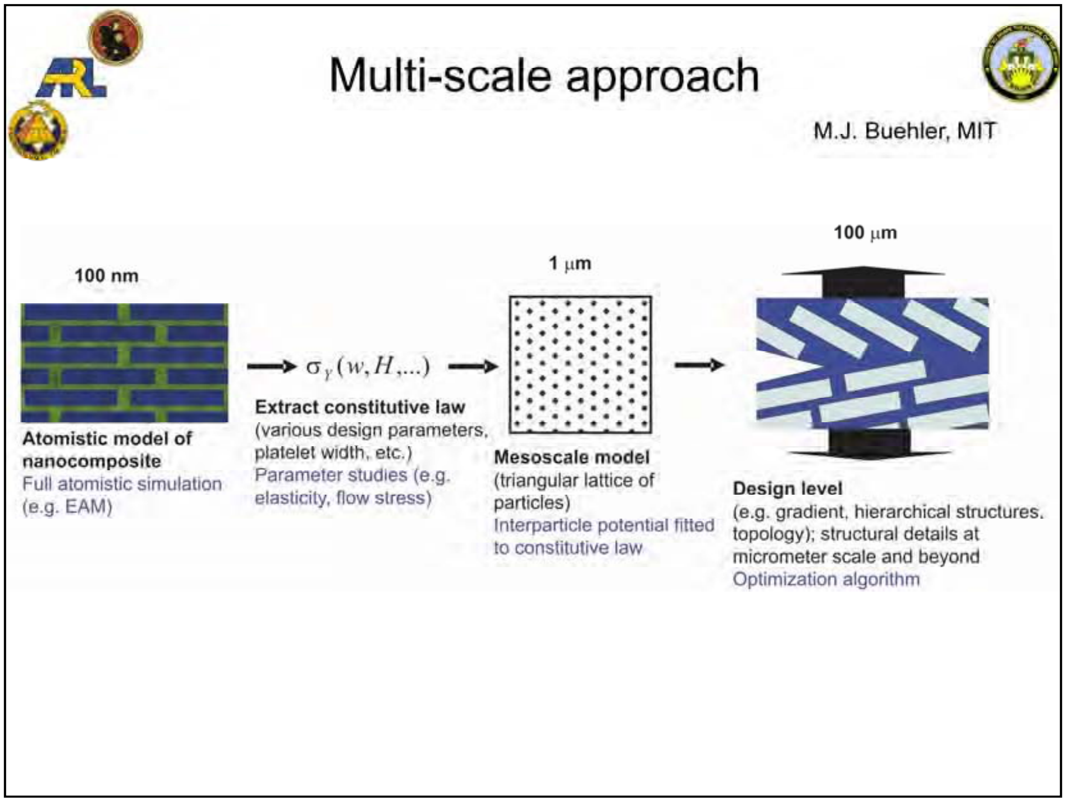


Is structural optimization at multiple length scales (=hierarchies) the key to combine disparate material properties?

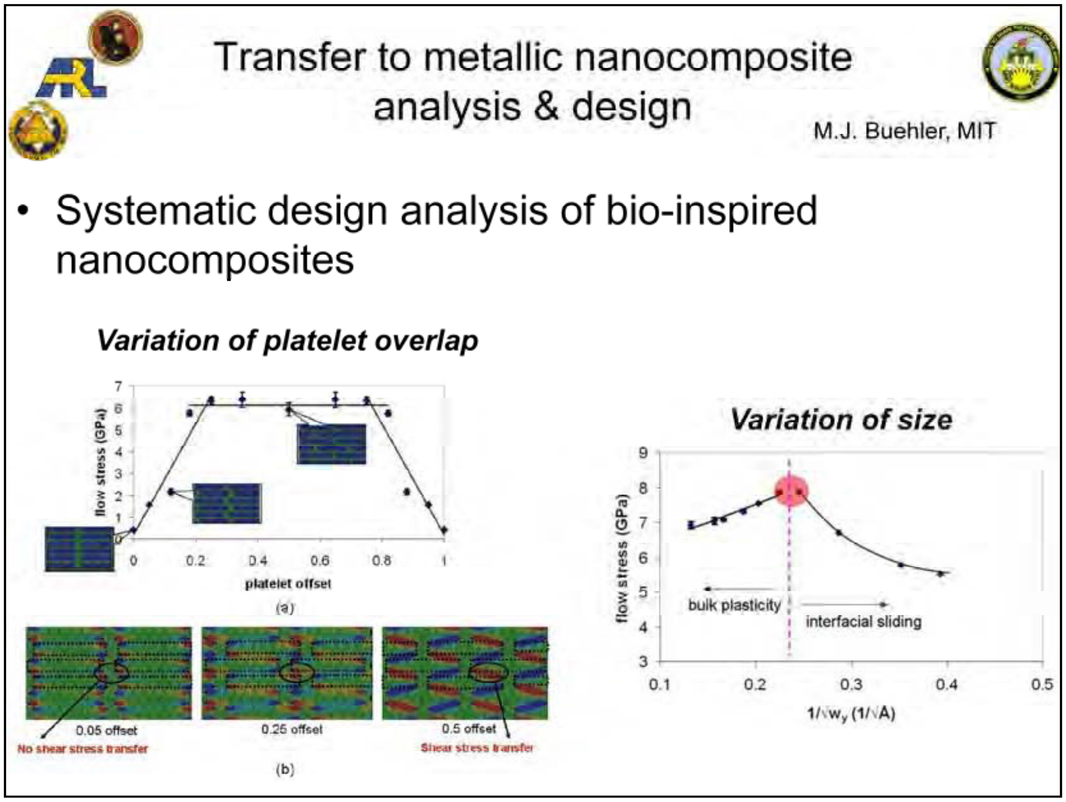
This slide illustrates how biological materials overcome the limitation of the "banana curve". A possible explanation may be the existence of material hierarchies. Our model (previous slide) illustrates this effect at a fundamental, atomistic and molecular level.



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-atomistic 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.

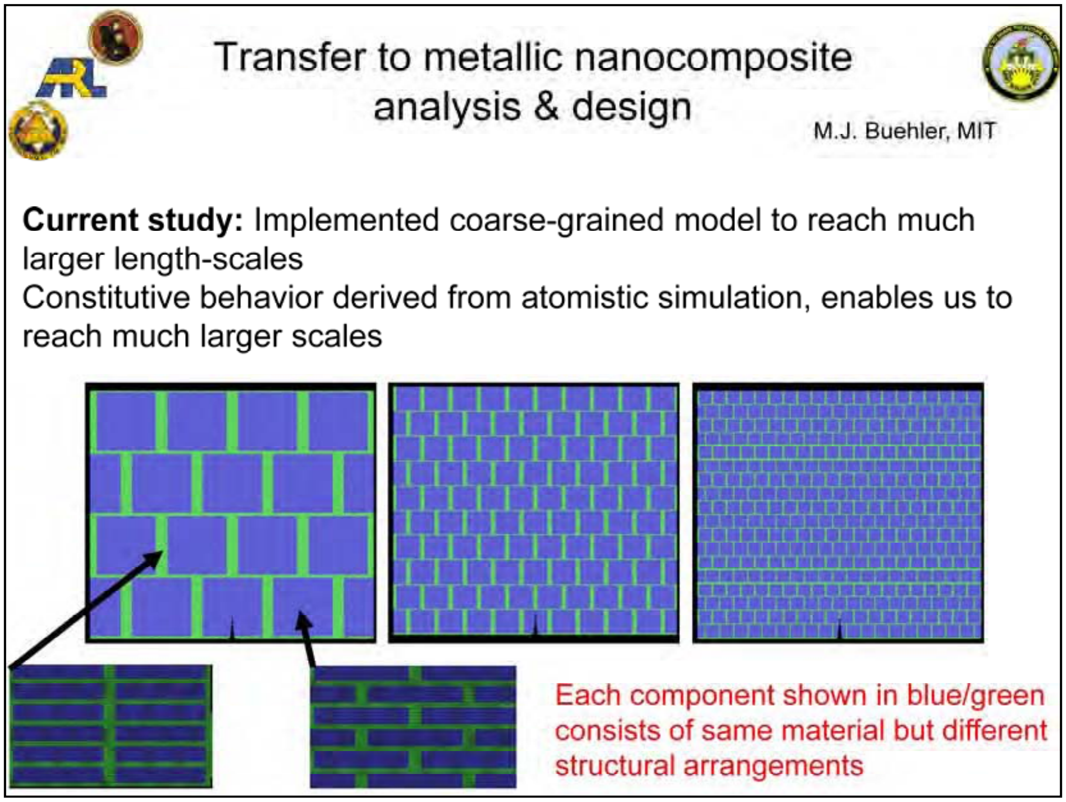
For example, the atomistic simulations reveal which shape, size, spacing of second phase platelets produces the maximum strength, and what changes in deformation mechanisms are seen across these geometric changes. A representative set of results will be reviewed in the next few slides.

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).

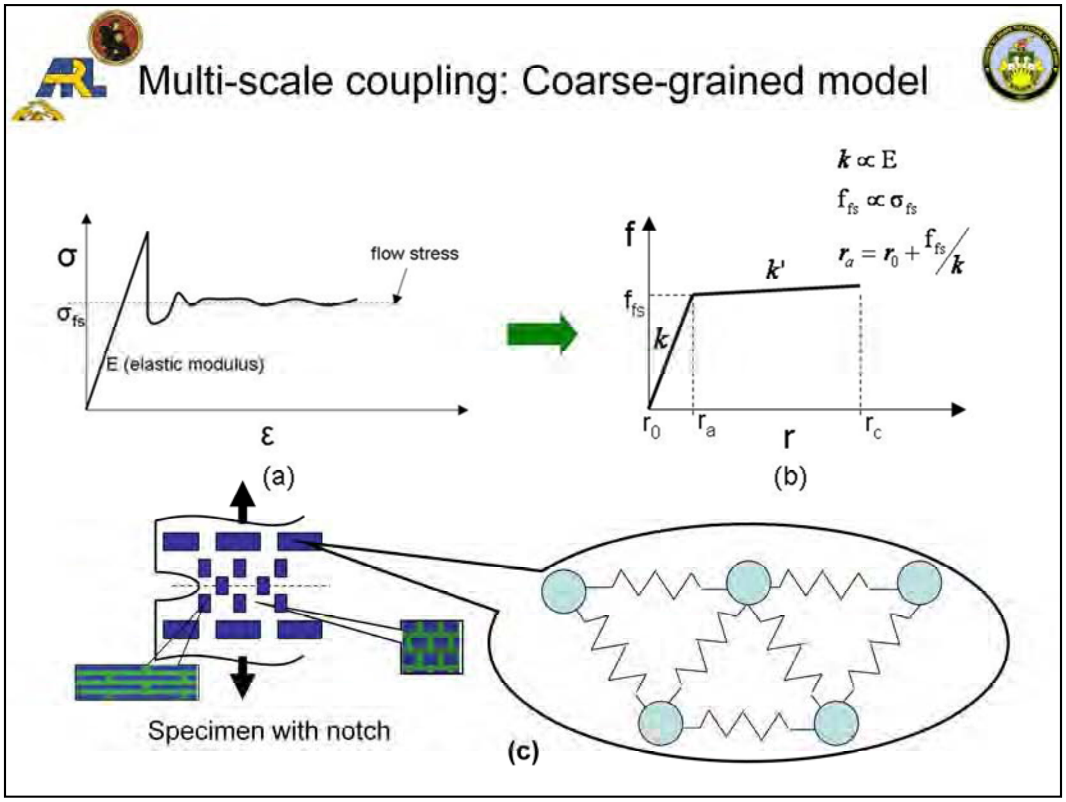
We have further discovered the critical geometric parameters for maximum yield stress at large deformation (D. Sen and M.J. Buehler, Acta Mat., submitted). The studies revealed mechanistic insight into the nanoscopic stress distribution and its relation to the toughening mechanism. This result is significant 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.

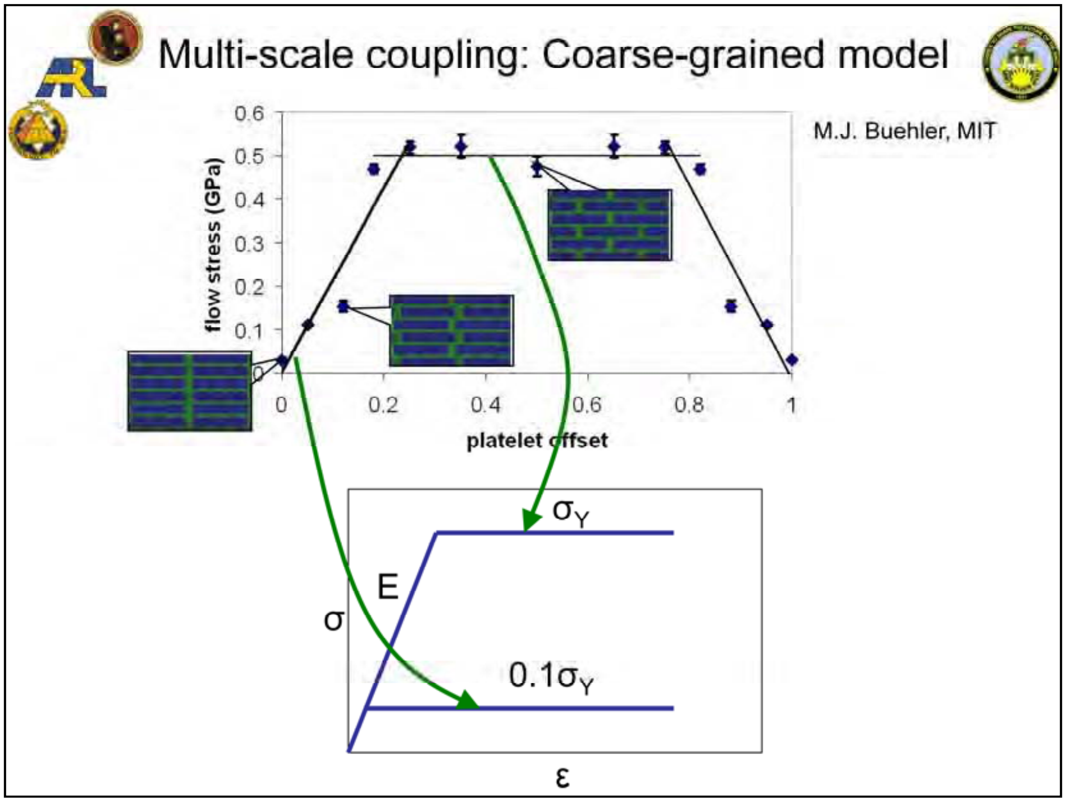
These results will guide laboratory processing techniques.



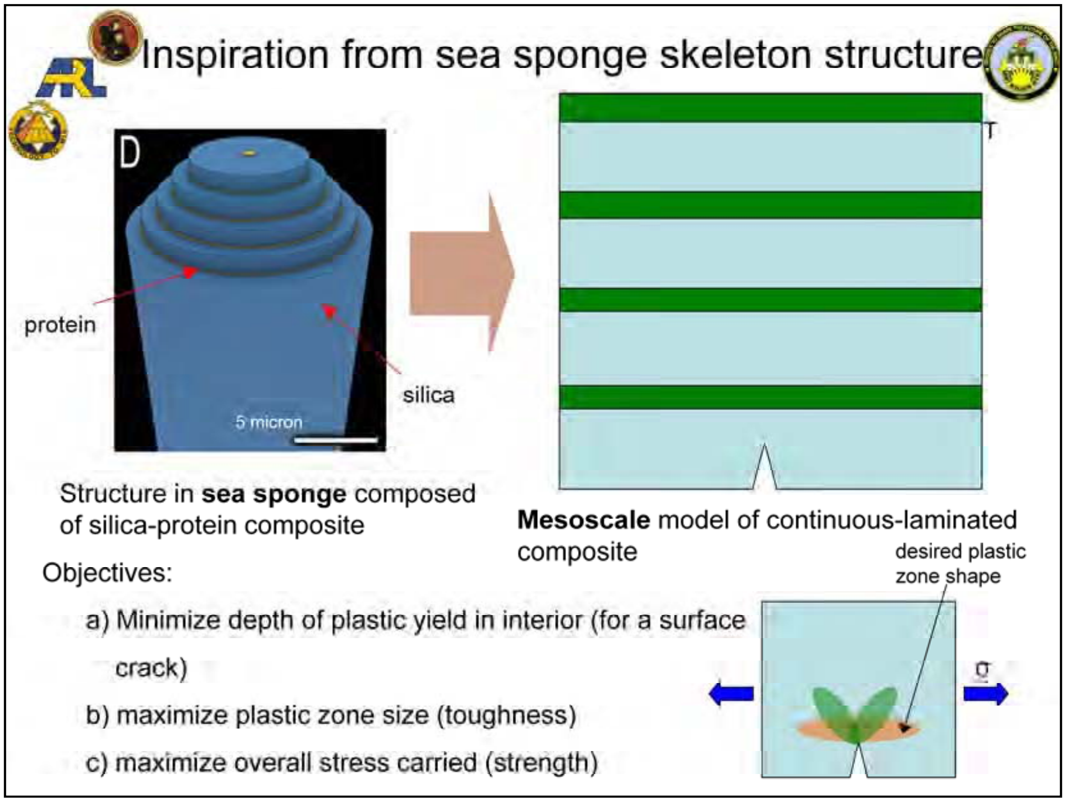
We have developed and tested a **mesoscale coarse-grained model** (similar to a finite difference method), which provides a bridge from atomistic to continuum length-scales. We are currently testing the performance of a variety of microstructural arrangements, where each phase shown here consists itself 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**.



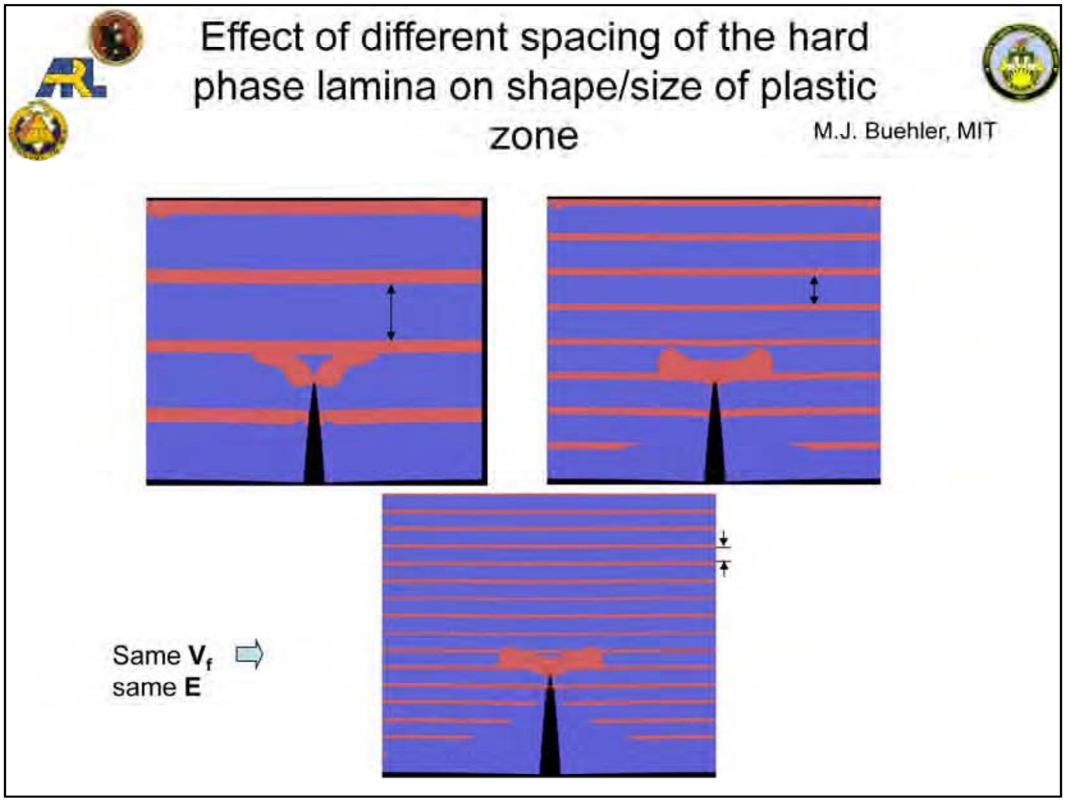
The details of the constitutive law for the coarse-grained system derived from fully-atomistic simulations. This force law is used for the coupling between scales of the two hierarchy levels. (a) shows the typical bulk uniaxial stress-strain behavior for a metallic nanocomposite structure, from which elastic modulus and flow stress can be derived; (b) shows a model \ being fit to this loading behaviour, 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.

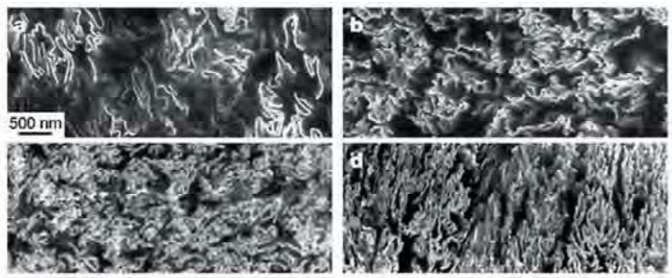


Preliminary results of the laminated 2-hierarchy composite. A surface crack is created under remote mode I loading. The volume fraction of the softer phase is 0.2 and constant in all systems, but the spacing ratio between layers is varied. The red region indicates all material that has yielded at a particular 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

M.J. Buehler, MIT

- Soft metal (Al, Cu) matrix – hard metal platelets (W)
- Soft metal (Al, Cu) matrix – ceramic platelets (Al_2O_3)
- Polymer matrix (PMMA/polystyrene) – CNT/graphene platelets

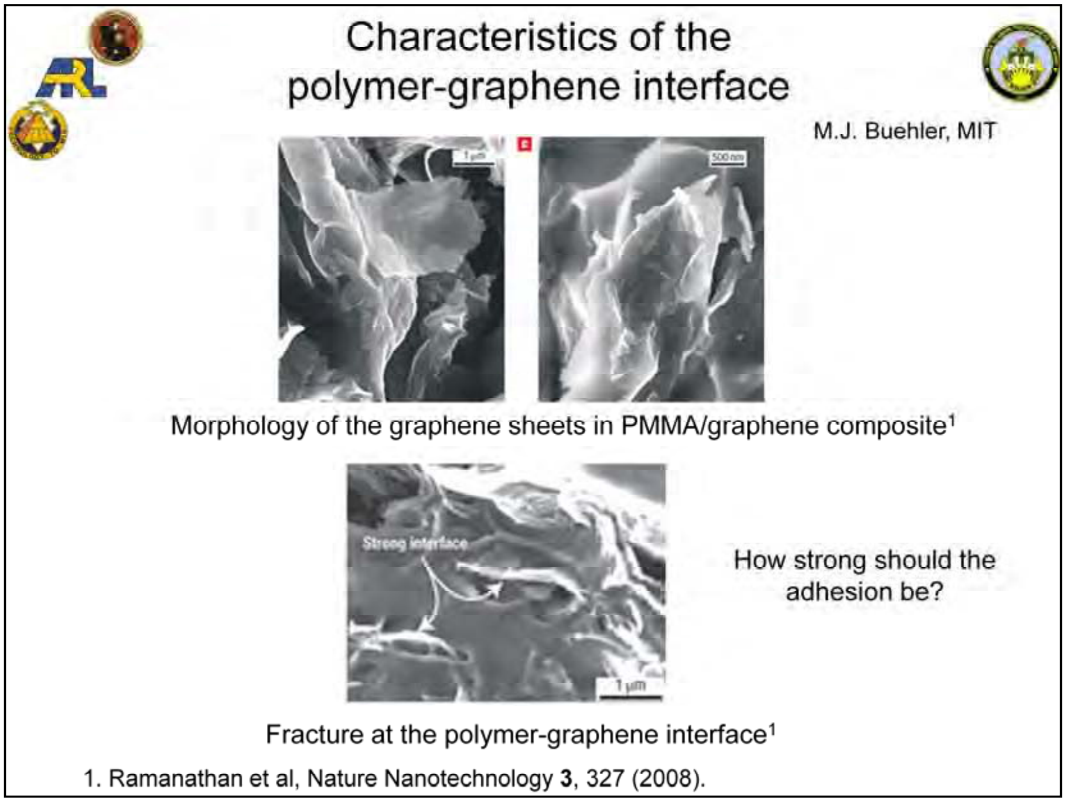


Polystyrene-graphene nanocomposites of different volume fractions[1]

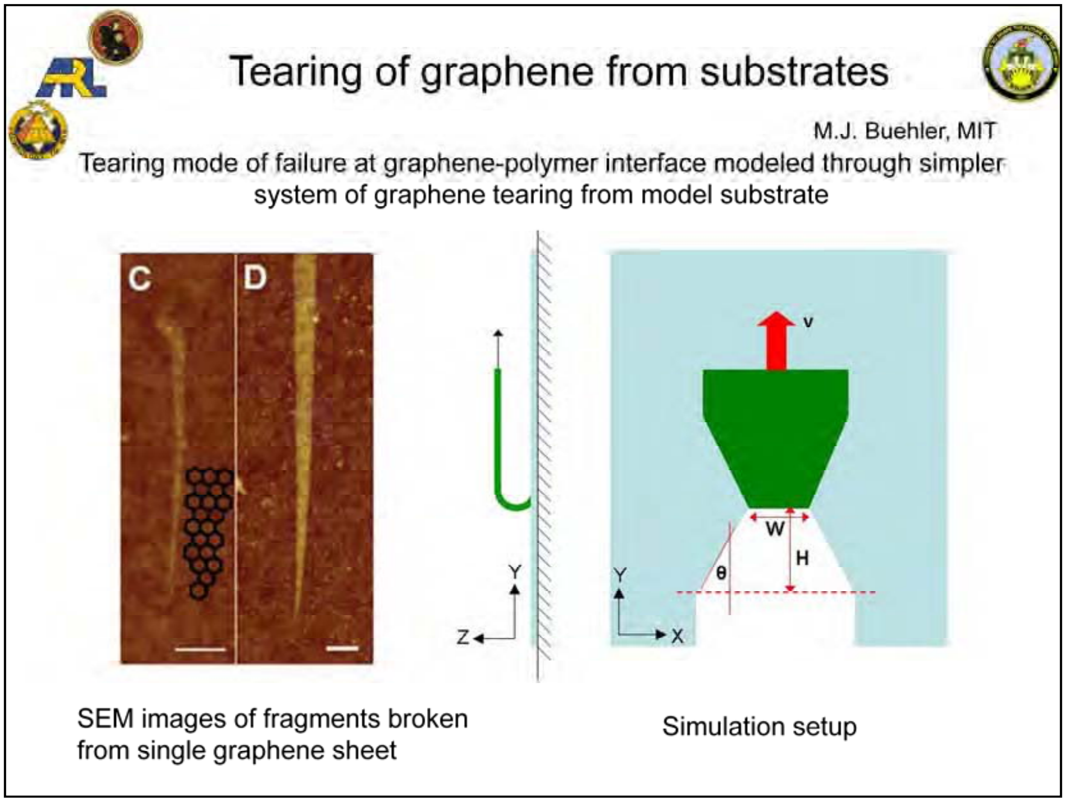
1. Stankovich et al, Nature **442**, 282 (2006).

M.J. Buehler, MIT

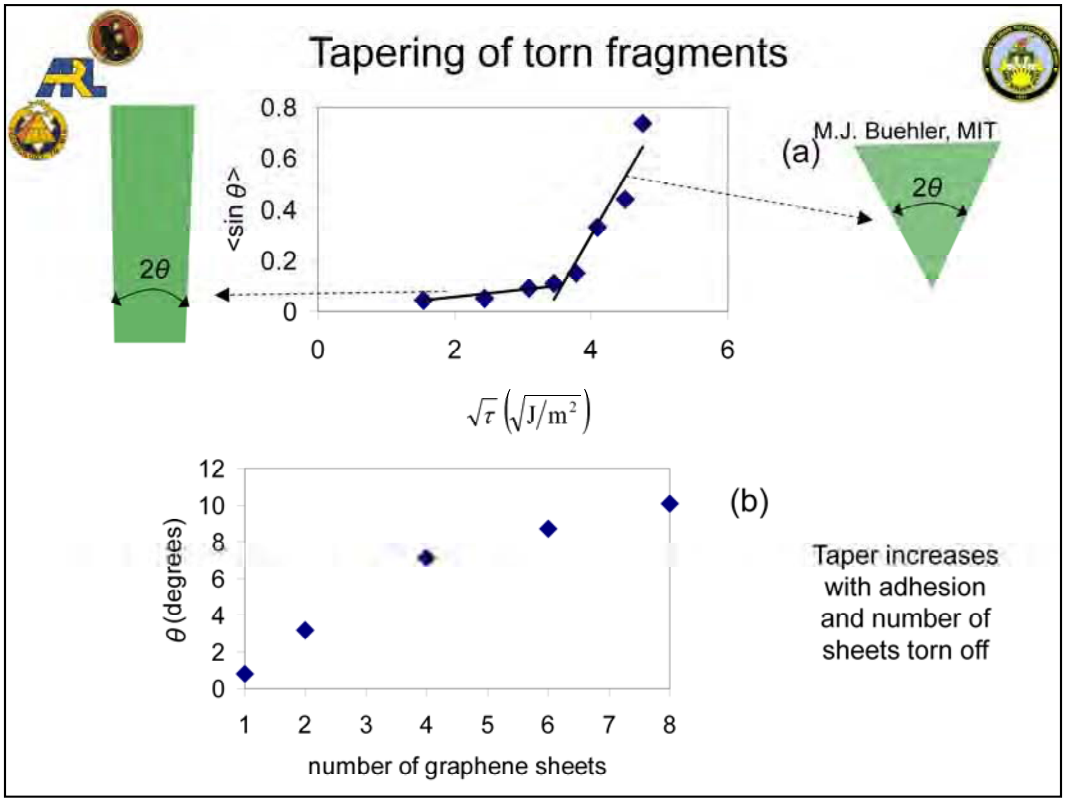
New concept: Graphene mechanics in extreme conditions



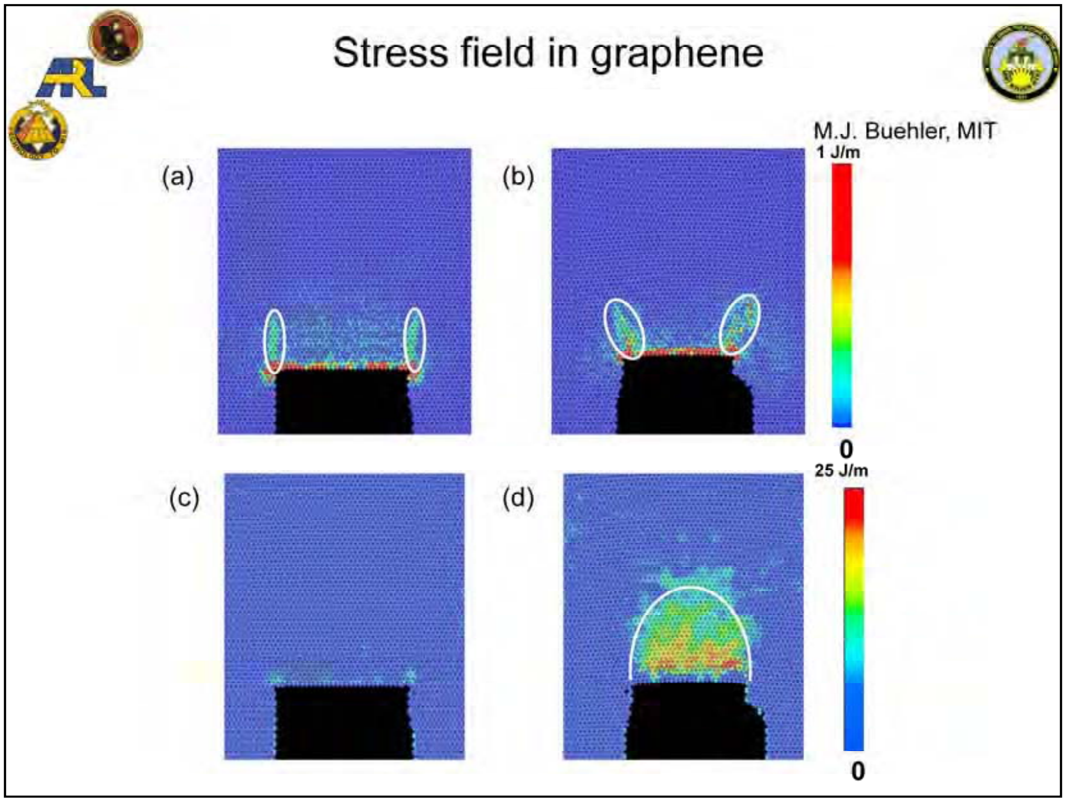
Persistent wrinkled nature of the functionalized graphene sheets within the composite provides for better interaction with the host polymer matrix. Lower figure shows fracture surface topography.



The strength of graphene-polymer interfaces is crucial to the overall load-carrying and failure mechanisms of the composite. A 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.

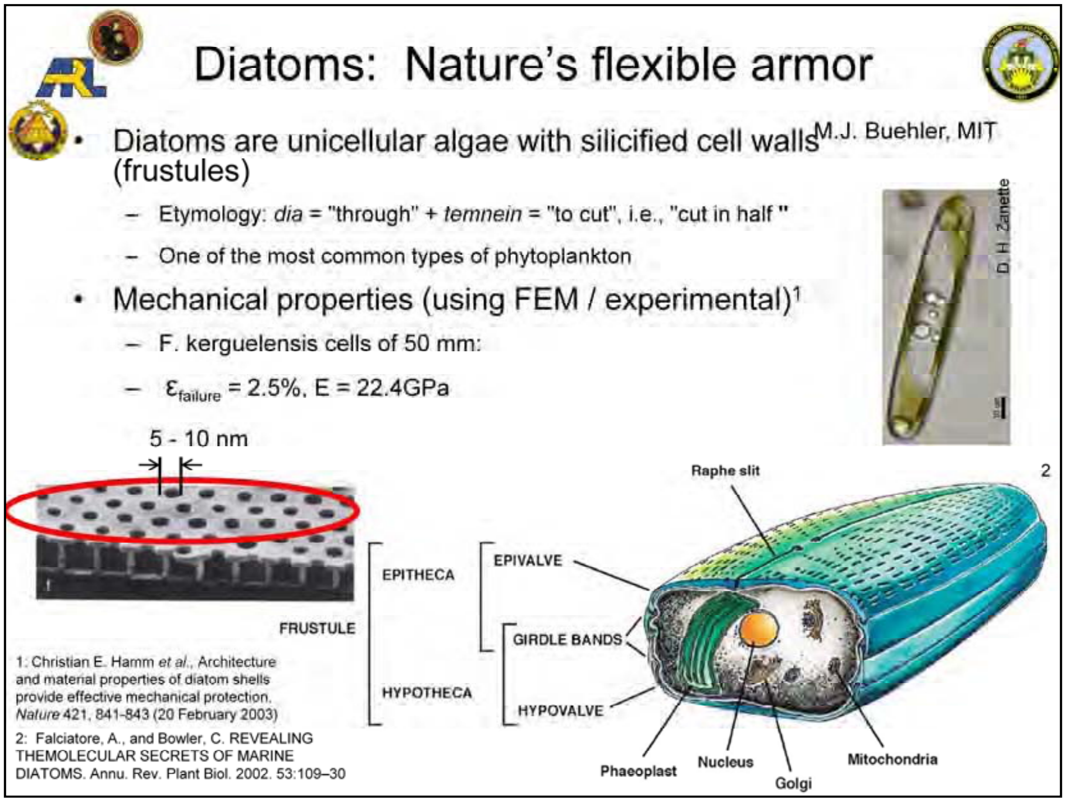


Shows the atomic level virial stresses for the graphene sheet (a) and (b) show the out-of-pane shear stress siggZX for weak and strong adhesion strengths of 2.4 and 20.2 J/m2 respectively; (c) and (d) show the in-plane tensile stress in Y direction siggYY for weak and strong adhesion strengths of 2.4 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.

M.J. Buehler, MIT

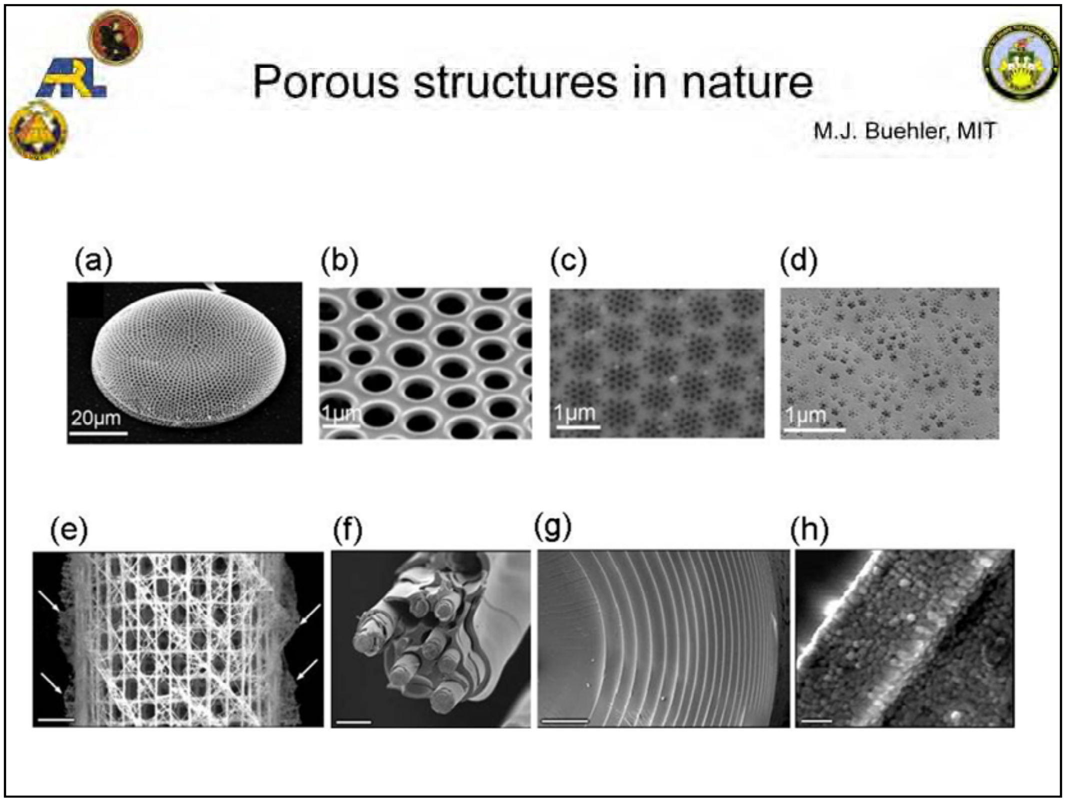
New concept: Biomimetic silicon

How to "transform" a brittle material (here as model selected silicon) into a ductile material…

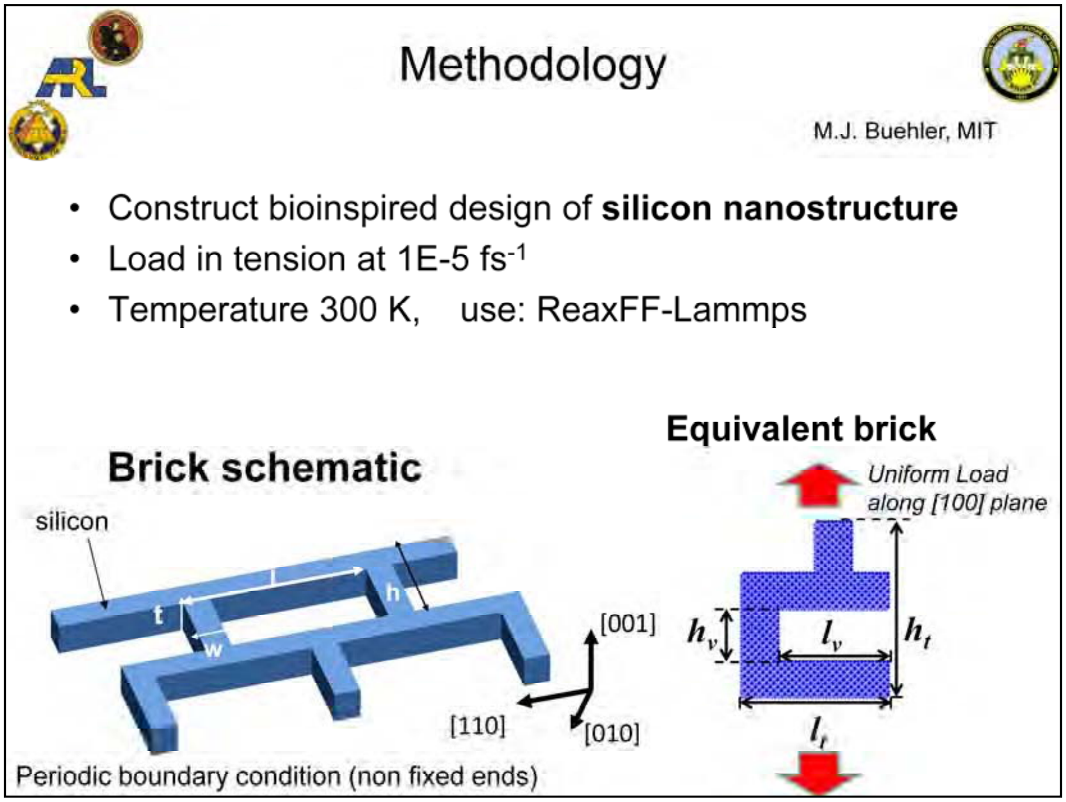


Overview of natural biological system, which shows the nanostructural arrangement of a brittle material (silica).

Can we interpret this design and use it for the design of new composites?

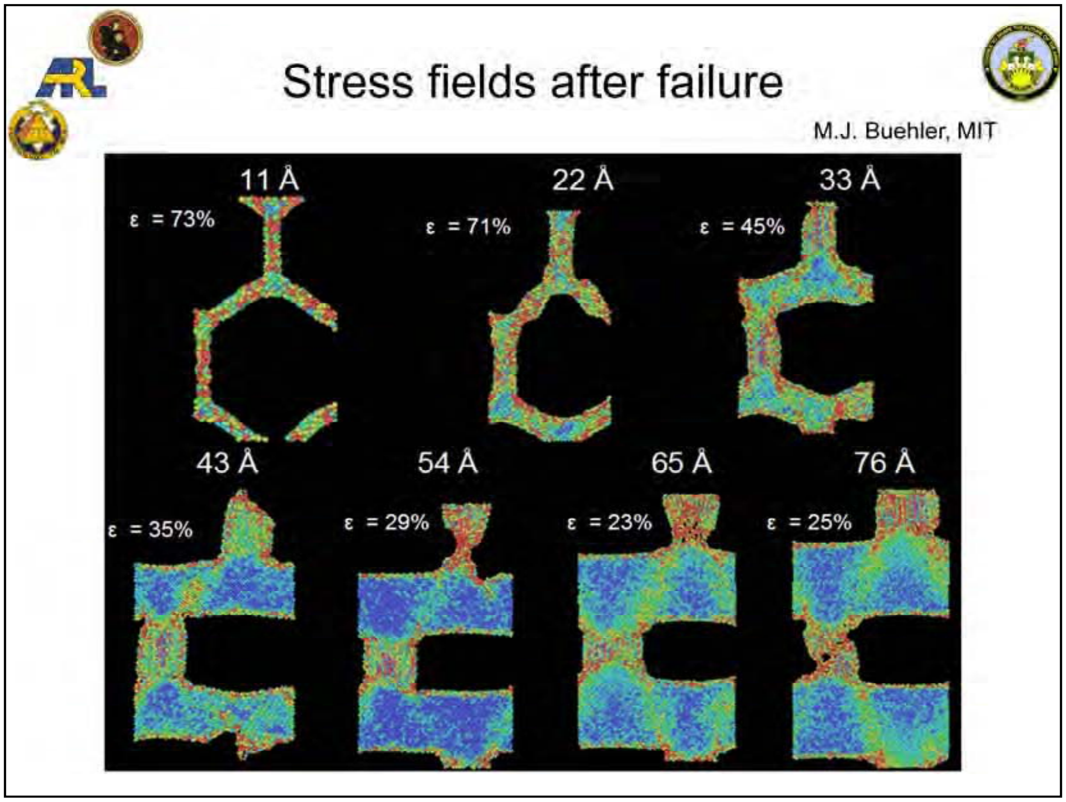


Structural hierarchies in two different silica-based skeletal assemblies in a marine diatom species (a-d) and a sea sponge (e-h). The diatom in (a) *Concinodicus sp.* has a silica-based exoskeleton (called frustule) made up of porous parts arranged in a hierarchical fashion (a) shows the whole frustule 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 constitutent 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.

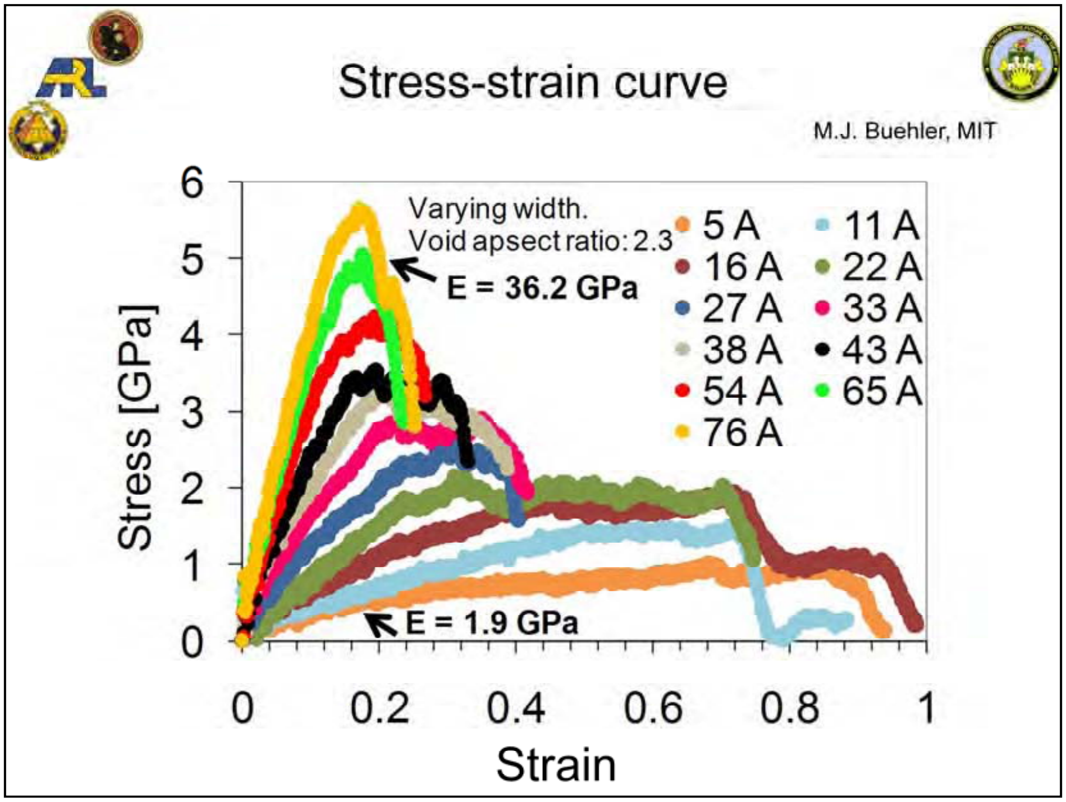


We have designed a first model system.

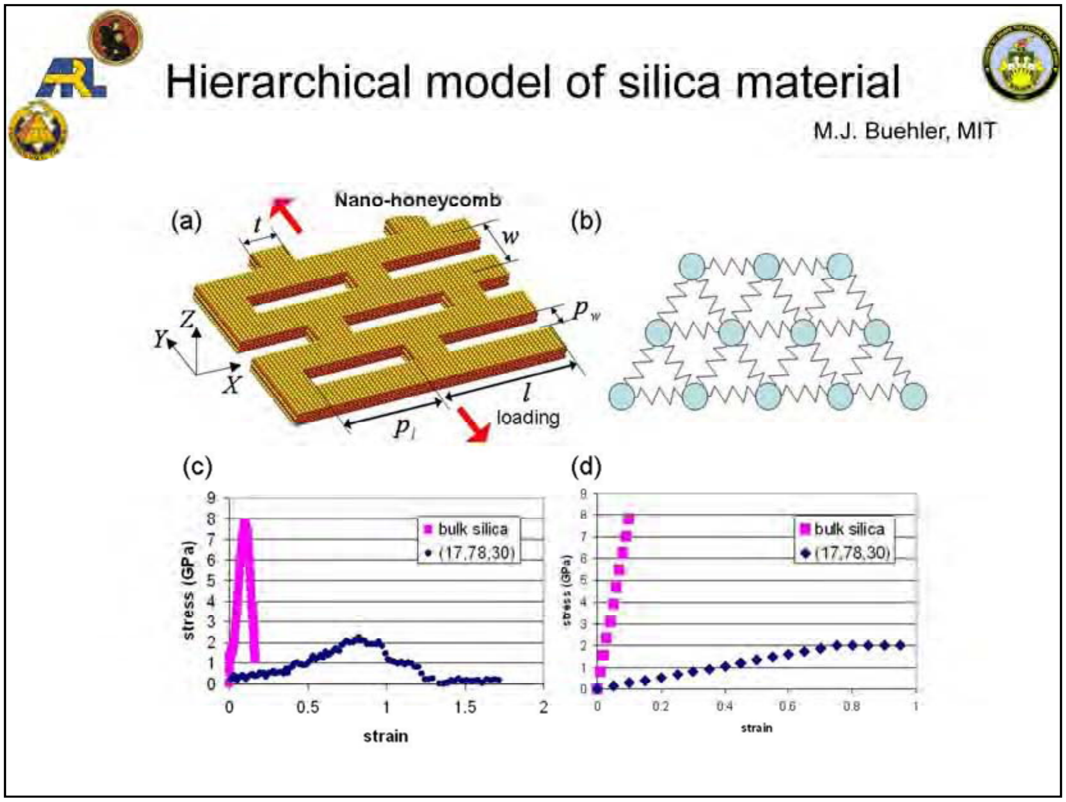
The following studies are focused on varying the width of the bricks and testing the influence on the mechanical behavior.



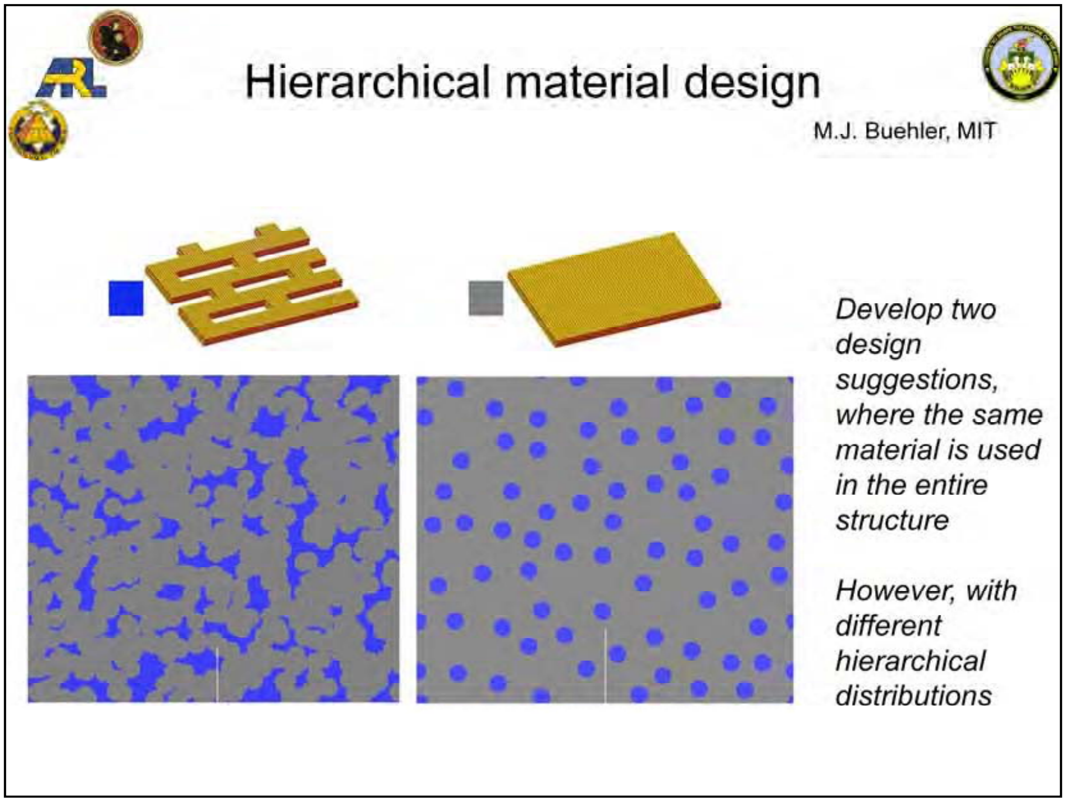
Results show that the larger systems feature a stress concentration at corners; smaller systems deform homogeneously.



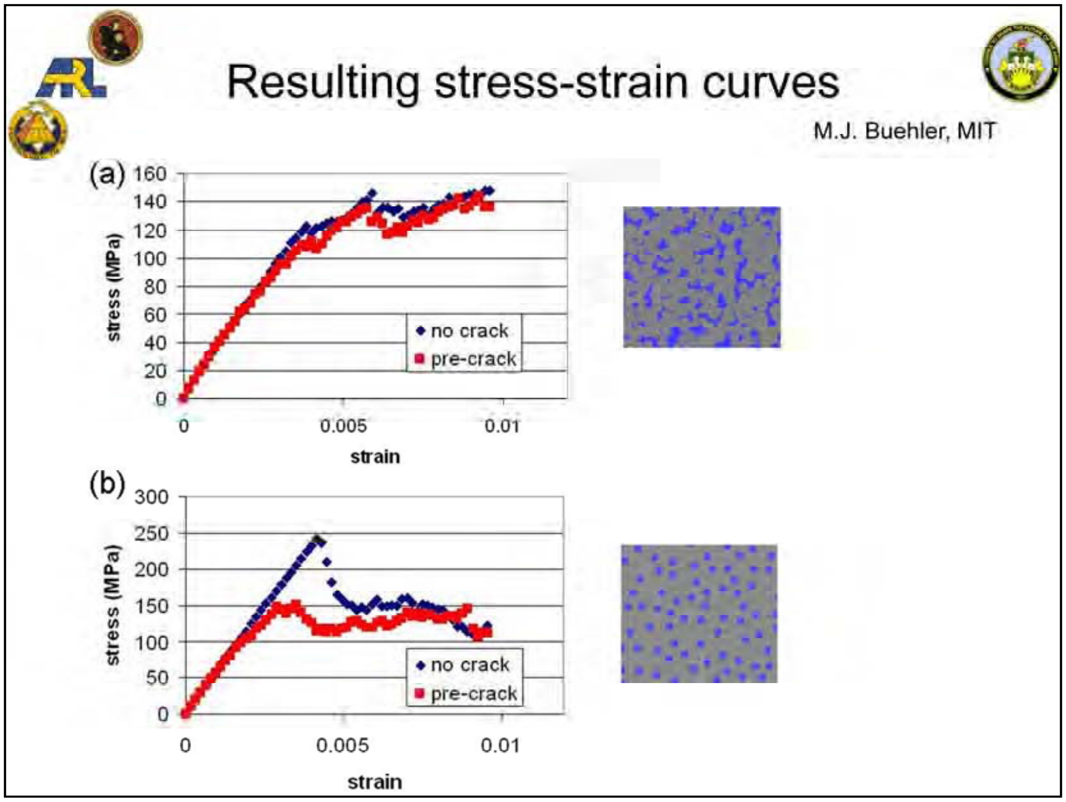
Results show that the smaller systems behave in a ductile fashion, and feature large deformation with >70% strain.



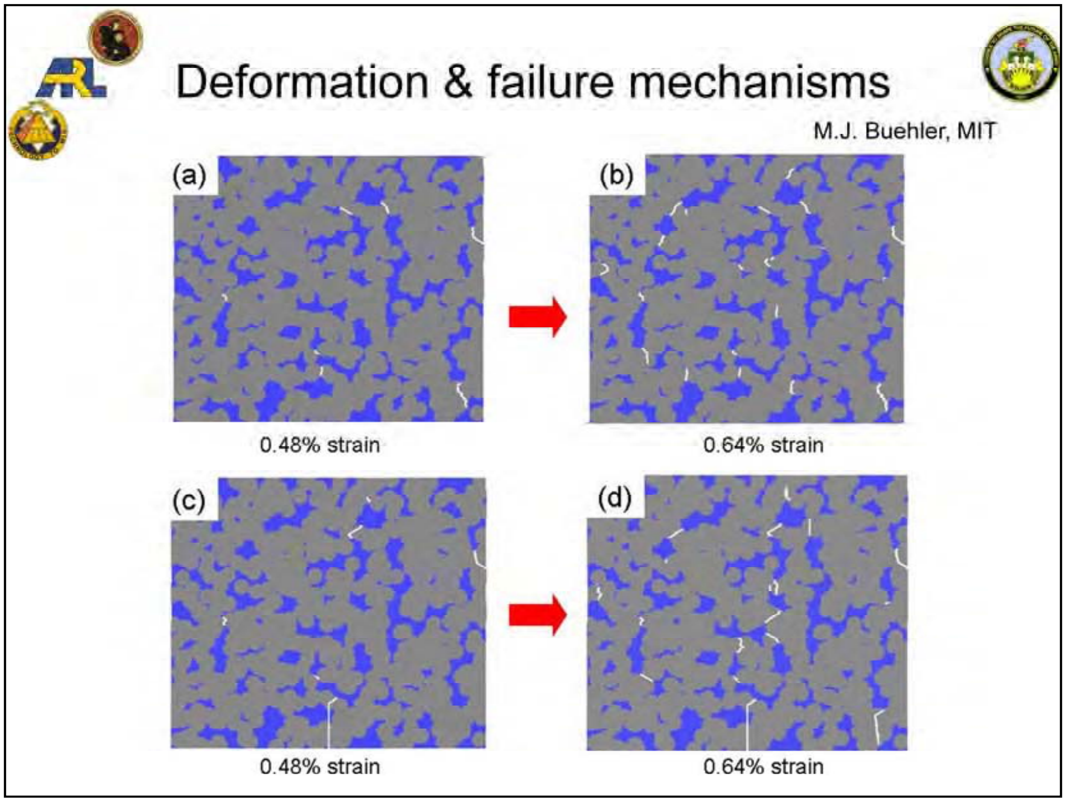
(a) shows the geometry of the nano-honeycomb used as building blocks for the composite structures, (b) shows a section of the triangular mesh mesoscale particle-spring model setup, (c) show stress-strain curves obtained from atomistic simulations of a nano-honeycomb structure, and for bulk silica with 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, pl, pw) 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.



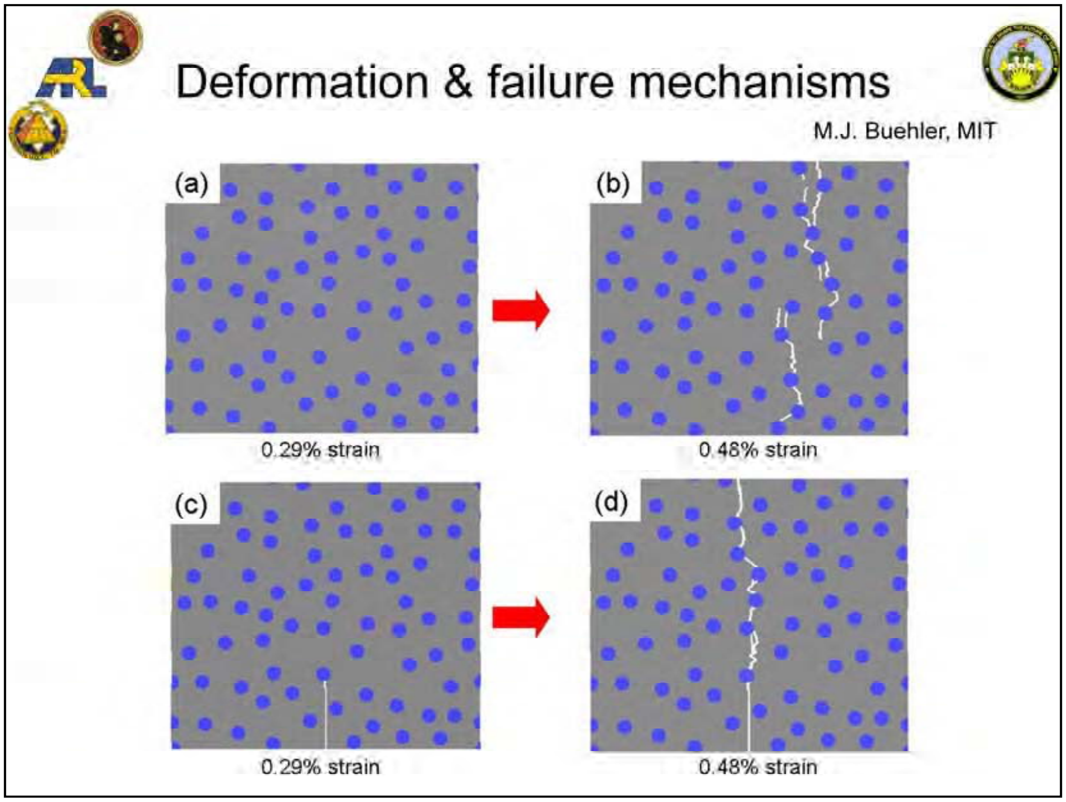
Randomly distributed particle composite structures at the mesoscale. Constituents are, bulk silica (in grey/light, with a high volume fraction) and nano-honeycomb structures (in blue/dark, small volume fraction). Design conditions that enhance toughness of bulk silica by distribution of small amount 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.



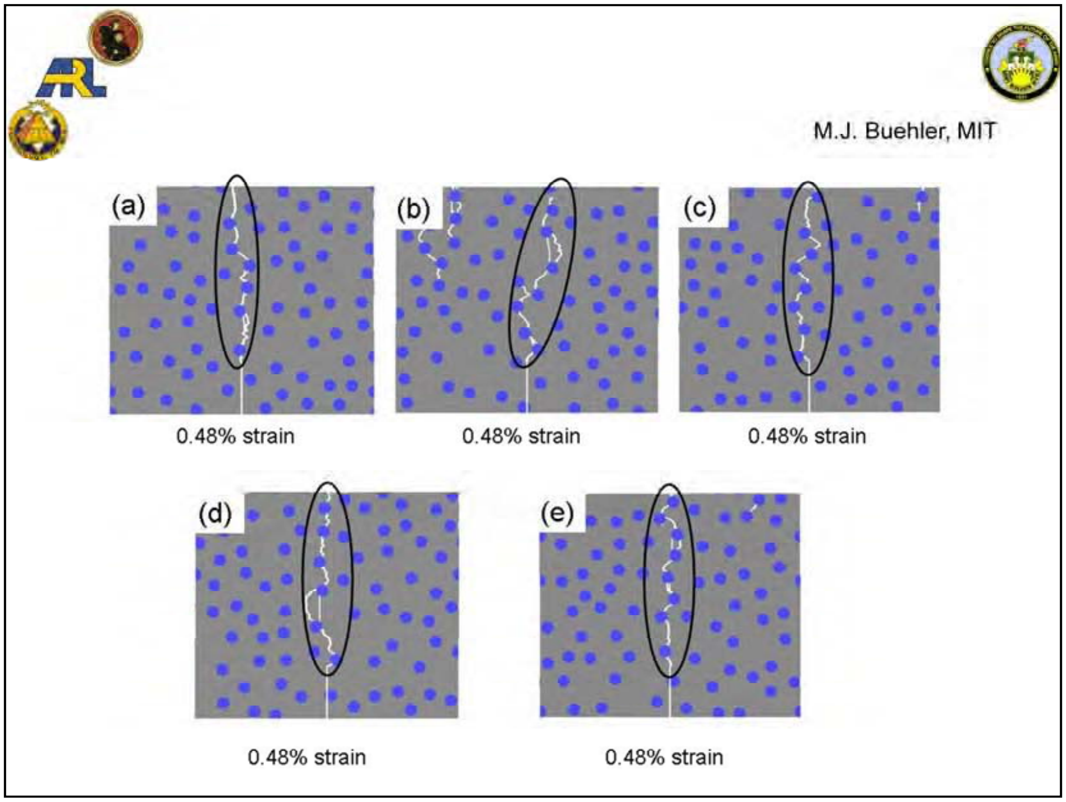
Stress-strain curves for (a) bulk-silica reinforcing composite structures, with and without presence of a pre-crack. The near-identical response shows the flaw-tolerance behavior for these structures to pre-cracks of the given size. The structures show multiple cracking throughout the material, and this 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.



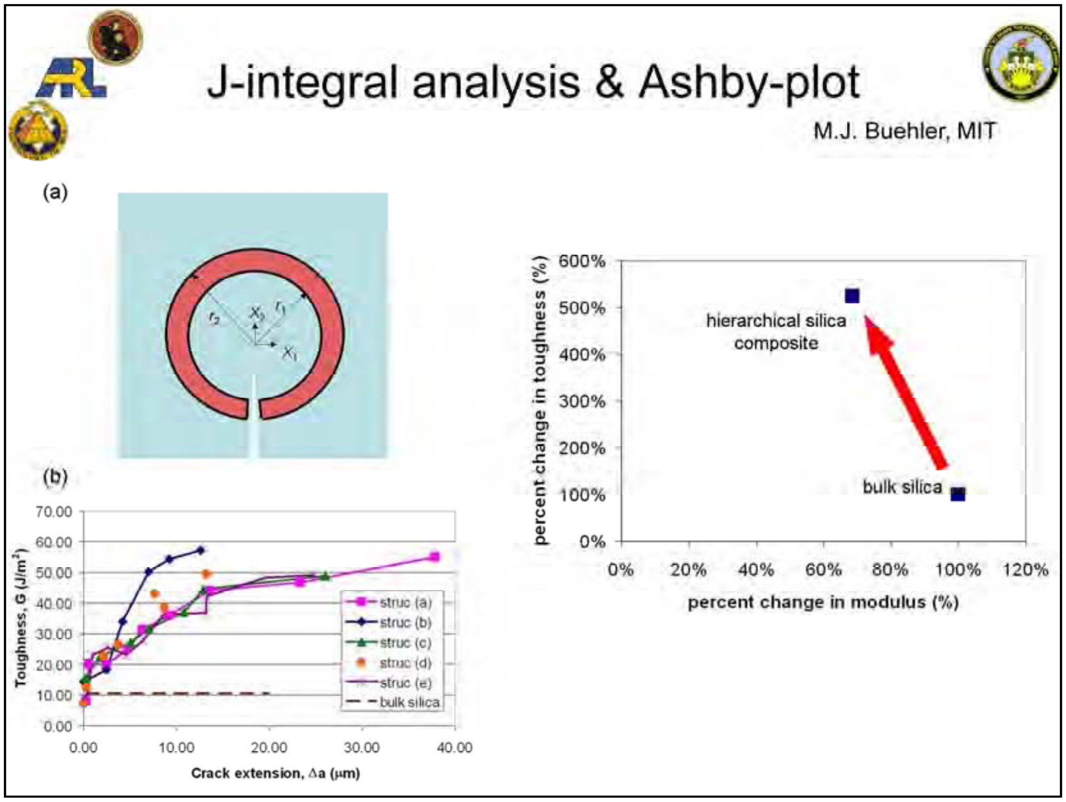
Crack pathways for composite structures with nano-honeycomb structure as the matrix and brittle silica as the reinforcing particulate phase. The volume fraction of silica phase is 76%. (a) and (b) show fracture progress starting from a material with no pre-crack; (c) and (d) show fracture progress in 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 undefected, and cracked structures (shown in Figure 4a). A fracture toughness cannot be measured for these structures and crack sizes.



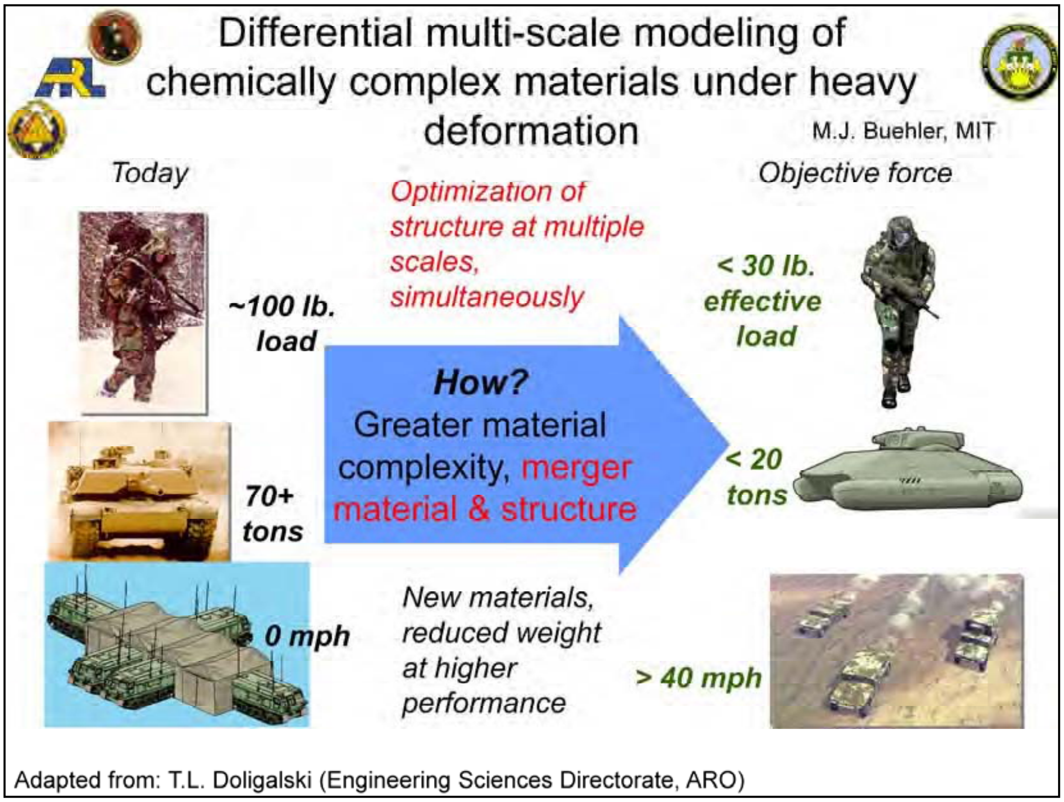
Crack pathways for composite structures with brittle silica as the matrix and nano-honeycomb structure as the reinforcing particulate phase. The volume fraction of bulk silica phase is 86%. (a) and (b) show fracture progress starting from a no pre-crack material; (c) and (d) show fracture progress from 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)

Massachusetts Institute of Technology

“**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)

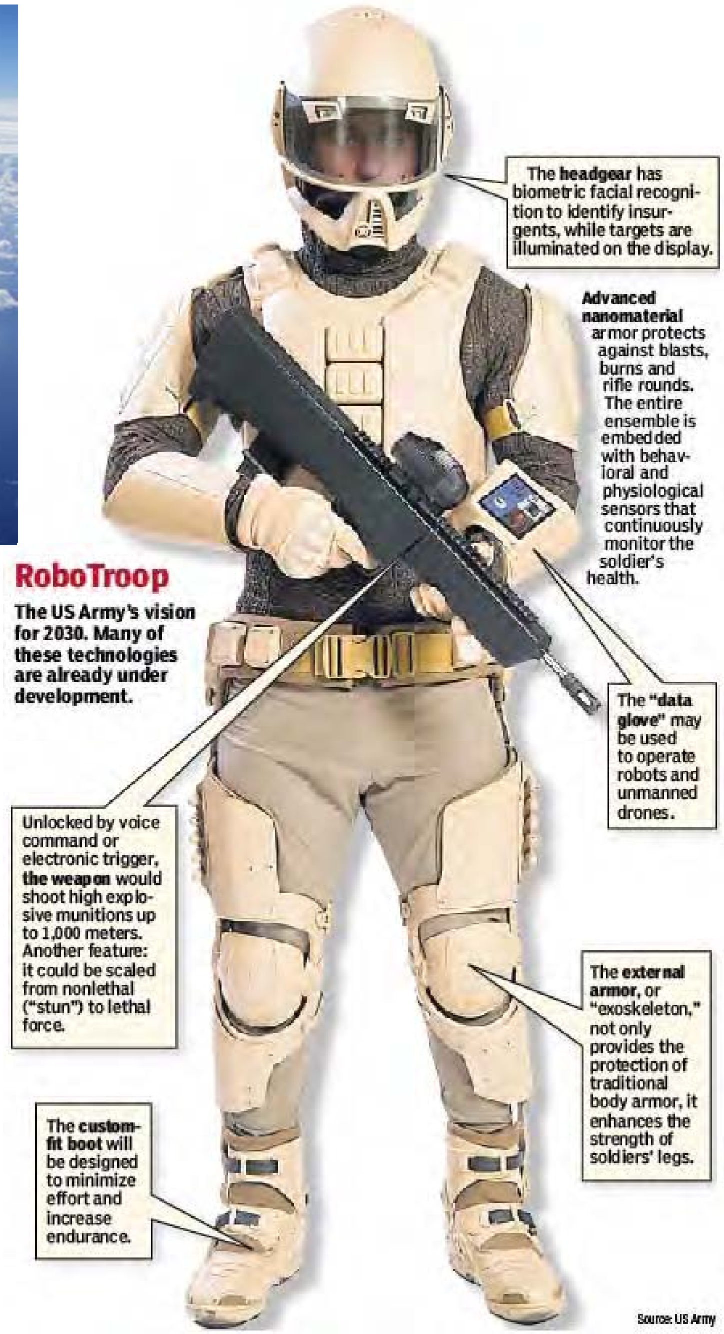
Have in abundance: natural materials

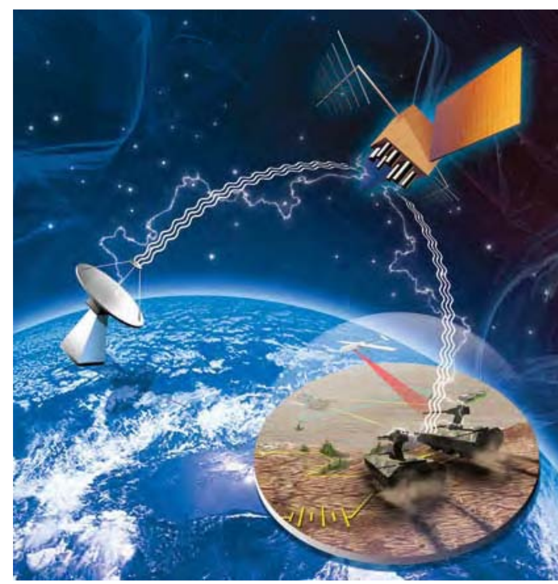
sand

water & rocks

soy beans (protein)

Need: functional materials, devices, armors…





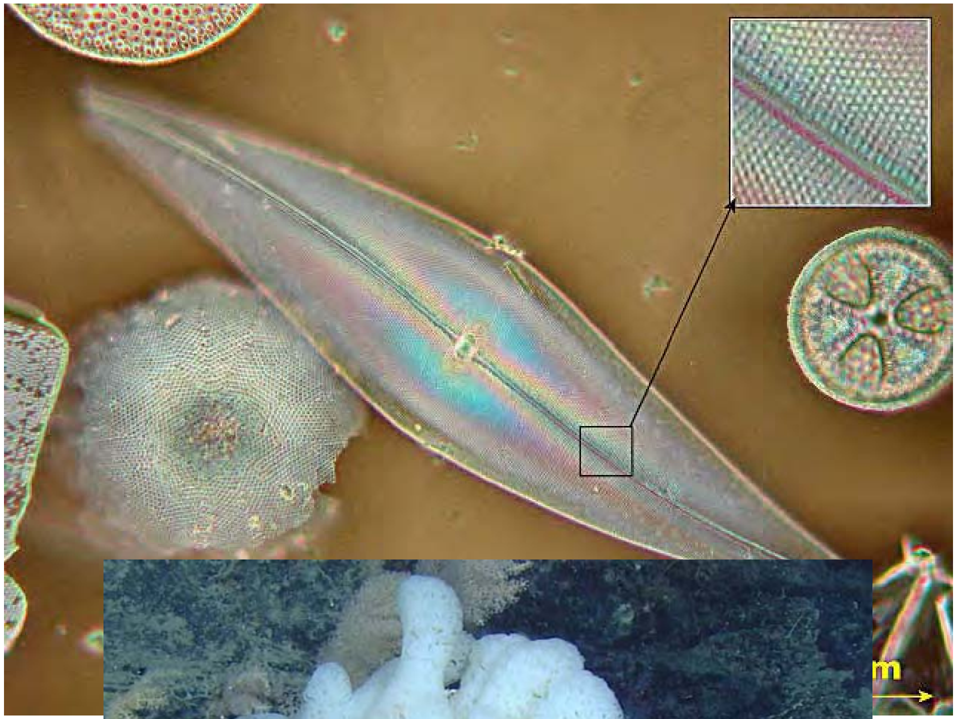
Core question: *How to turn abundant materials into functional materials?*

?????

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

Path to success – understand biological materials

Biological highly functional materials – *diatoms, sea sponges, organisms*

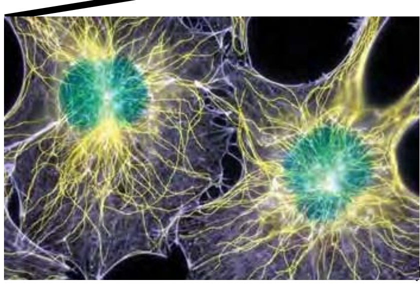


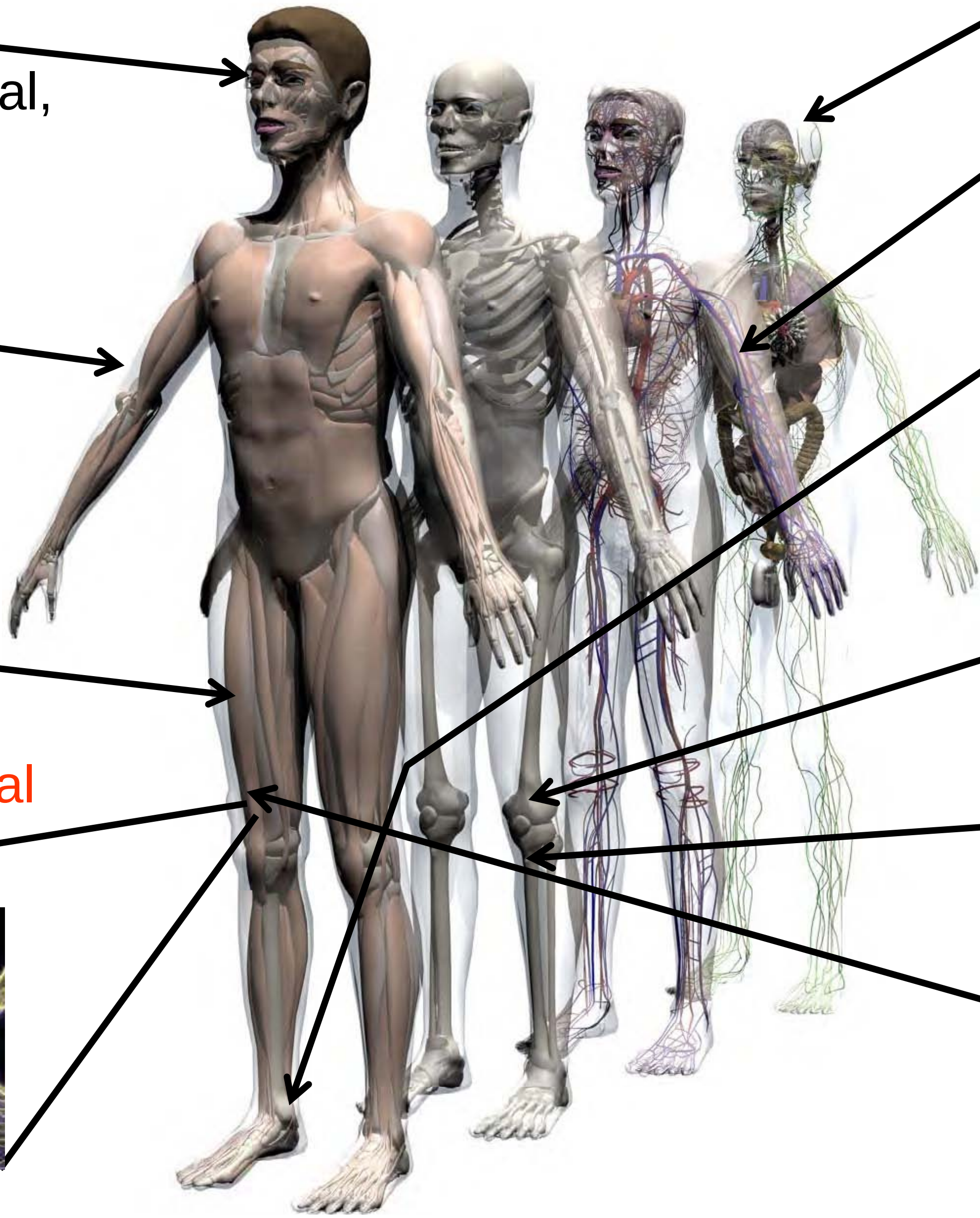
Protein materials in biology

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)

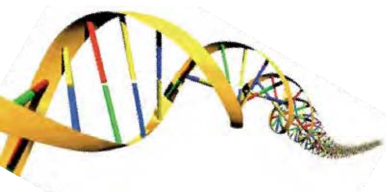
Cartilage (reduce friction in joints)

Bone (structural stability, collagen/minerals)

Muscle tissue (mechanical force, motor proteins)

http://www.humanbody3d.com/ and http://publications.nigms.nih.gov/insidethecell/images/ch1_cellscolor.jpg

Genes (DNA structure) define protein structure



ACGT →

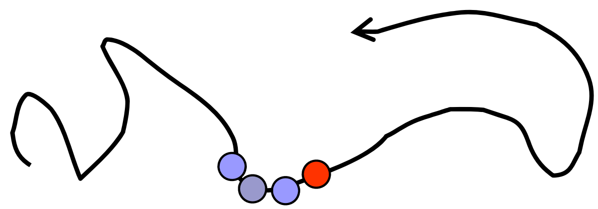
Four letter code "DNA"

Combination of 3 DNA letters equals a amino acid

E.g.: Proline –

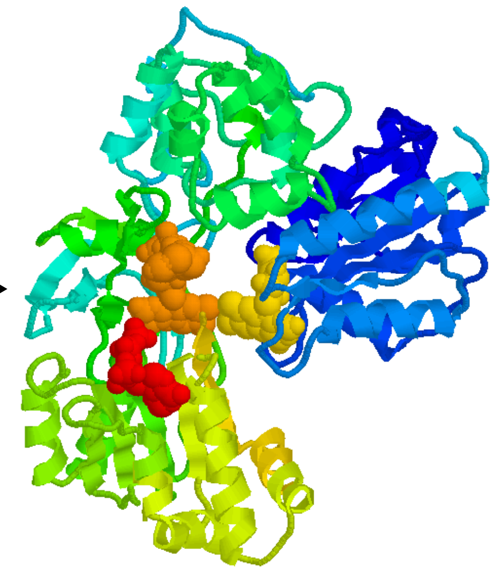
CCT, CCC, CCA, CCG

Transcription/ translation



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

Sequence of amino acids "polypeptide" (1D structure)



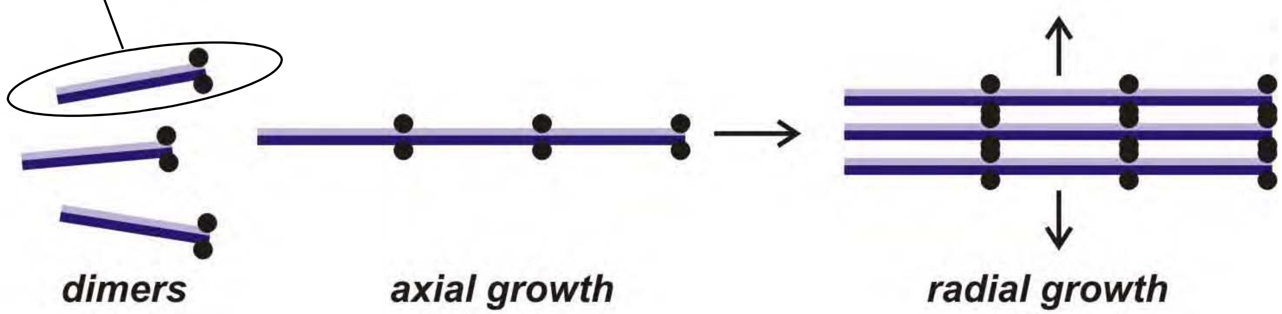
Folding (3D structure)

M. Buehler *et al*., *Nature Materials*, 2009

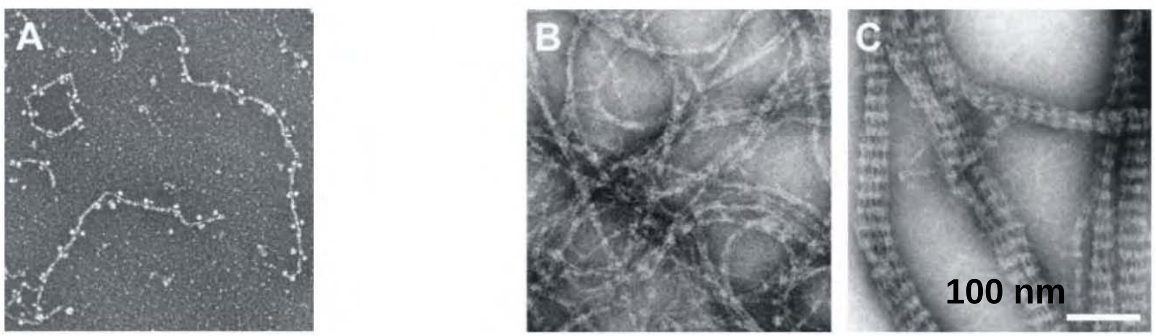
Protein material assembly

Folded protein

intermediate filaments



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



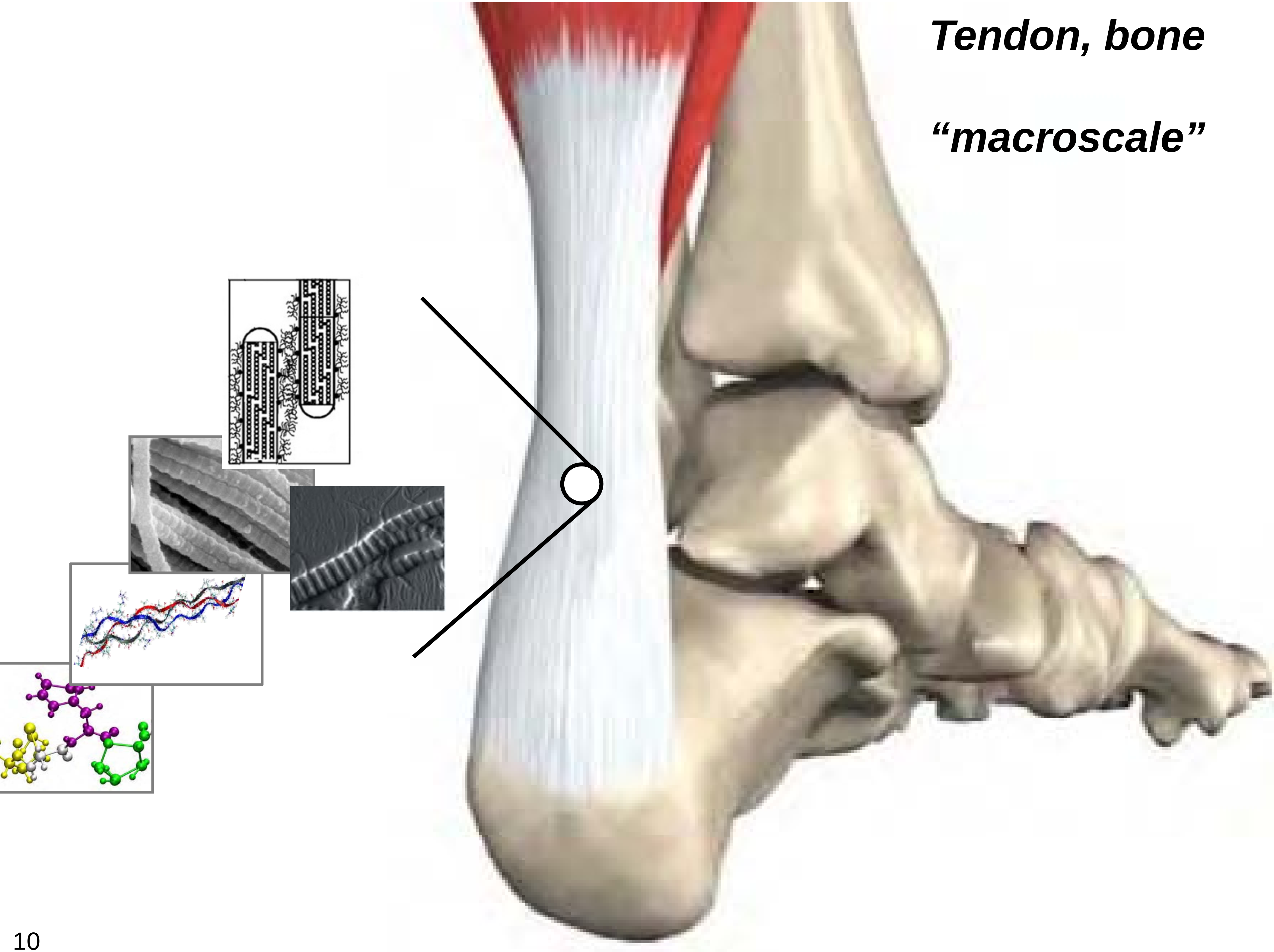
Experimental analysis
(Herrmann, Aebi, Kreplak *et al.*)

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

M. Buehler *et al.*, *Nature Materials*, 2009

Tendon, bone

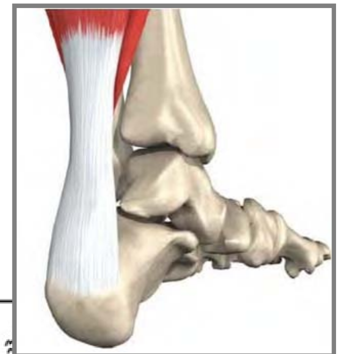
"macroscale"



Collagenous tissues – an issue (tissue) of multiple scales

macro

Tissues (tendon, bone)
dimension ≈ cm



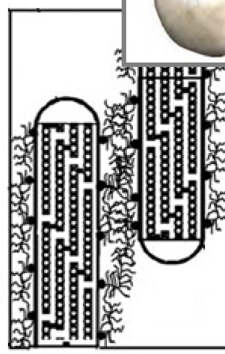
Bone

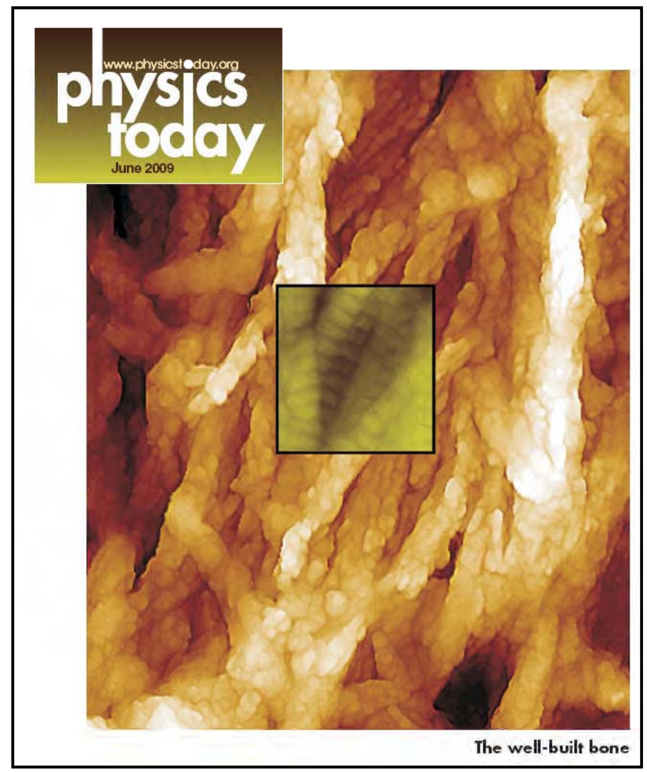
Tendon

Cartilage

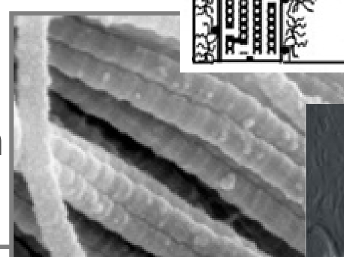
Eye's cornea

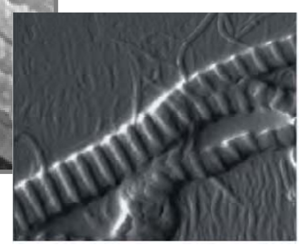
Collagen fiber
length ≈ mm
diameter ≈ 10 μm



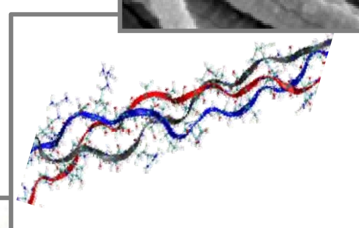


Collagen fibril
length ≈ μm
diameter ≈ 100 nm

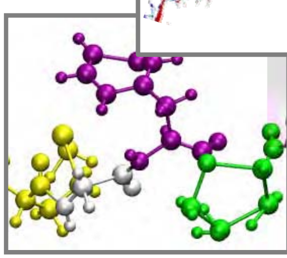




Collagen molecule
length ≈ 300 nm
diameter ≈ 1.6 nm



Amino acids
covalent bond ≈1 Å



nano

M.J. Buehler, *Proc . Nat'l Academy of Sciences USA,* 2006; R. Ritchie, M. Buehler, P. Hansma, *Physics Today*, 2009

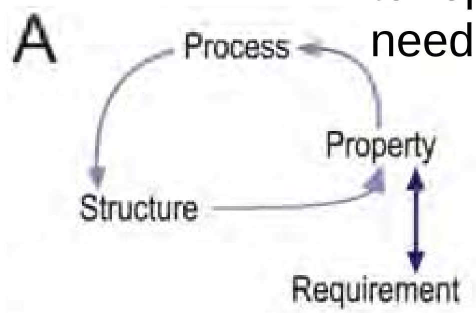
Biological materials are adaptable, mutable…

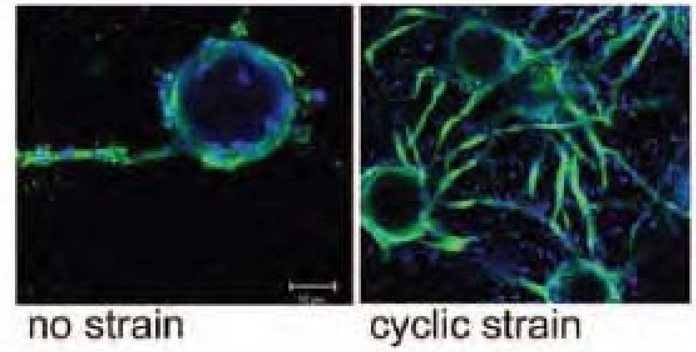
Biological systems universally feature active components; e.g.: bone remodels according to changes in loading, cells change their shape under different environments or stress

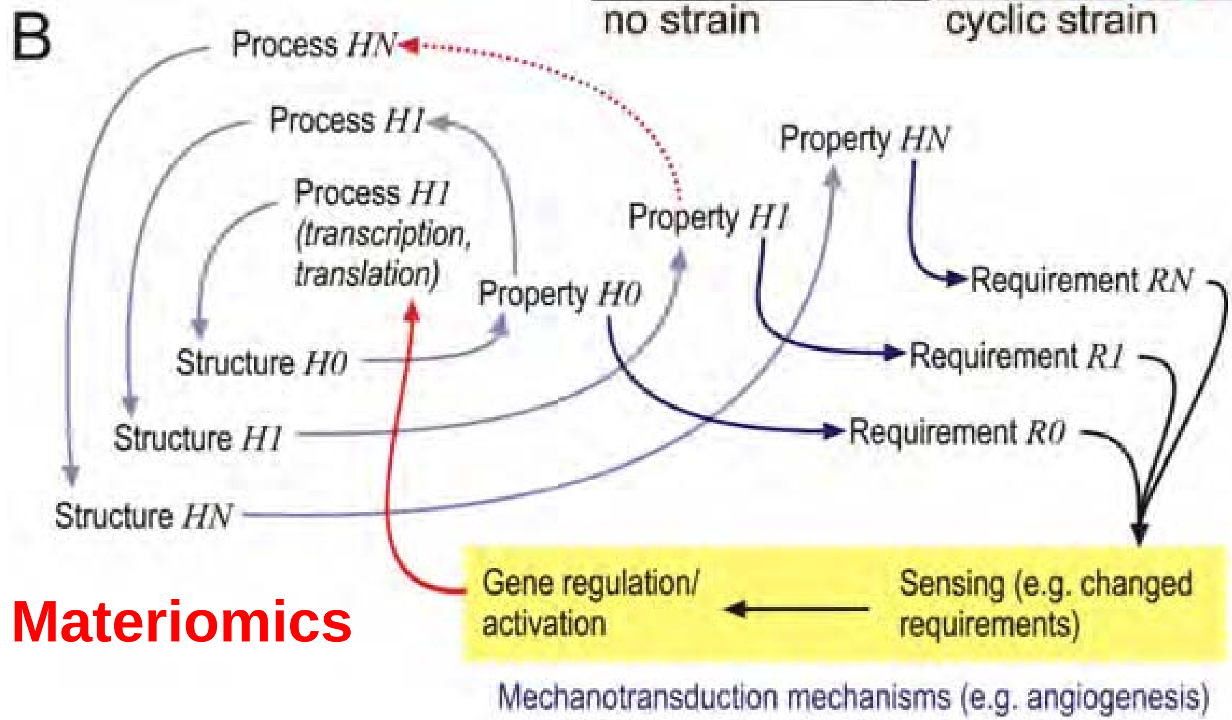
Mechanisms: Sensing of environmental cues followed by gene regulation/activation, which changes the hierarchical structure of materials ("mutability")

Buehler and Yung, *Nature Materials*, 2009

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







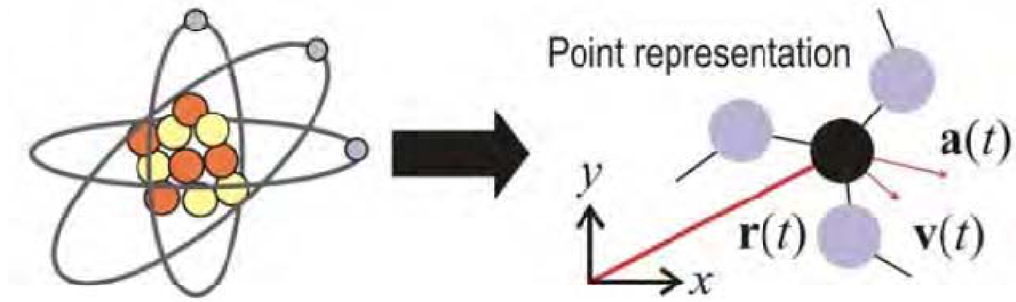
Materiomics

Y. Yung, M. Buehler, D. Mooney, *et al.*, *PNAS,* 2009

Challenge: Time-scales on the order of minutes, hours, days

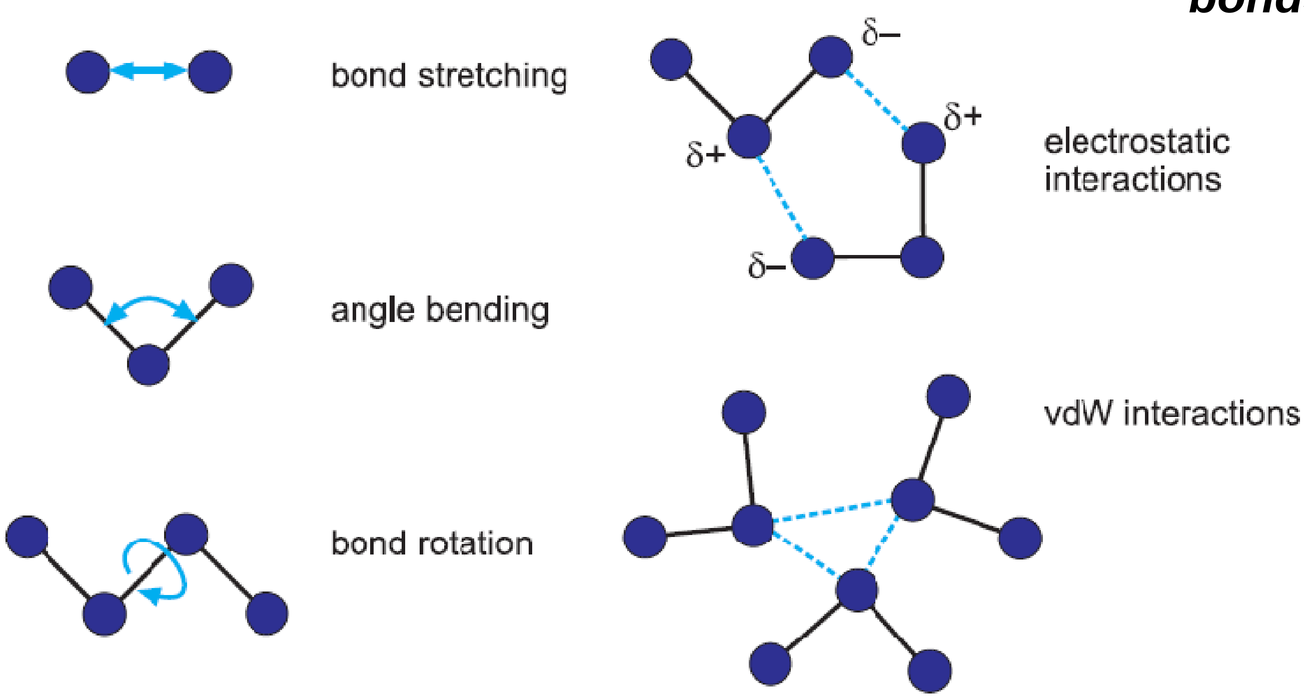
Linking chemistry, structure and mechanics

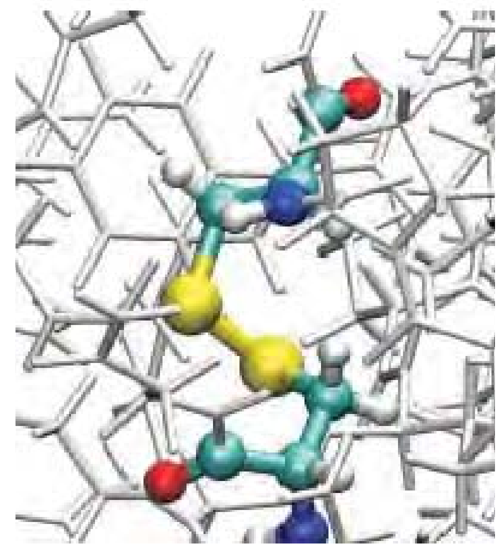
Molecular dynamics:
Fundamental model of materials
"bottom-up"



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

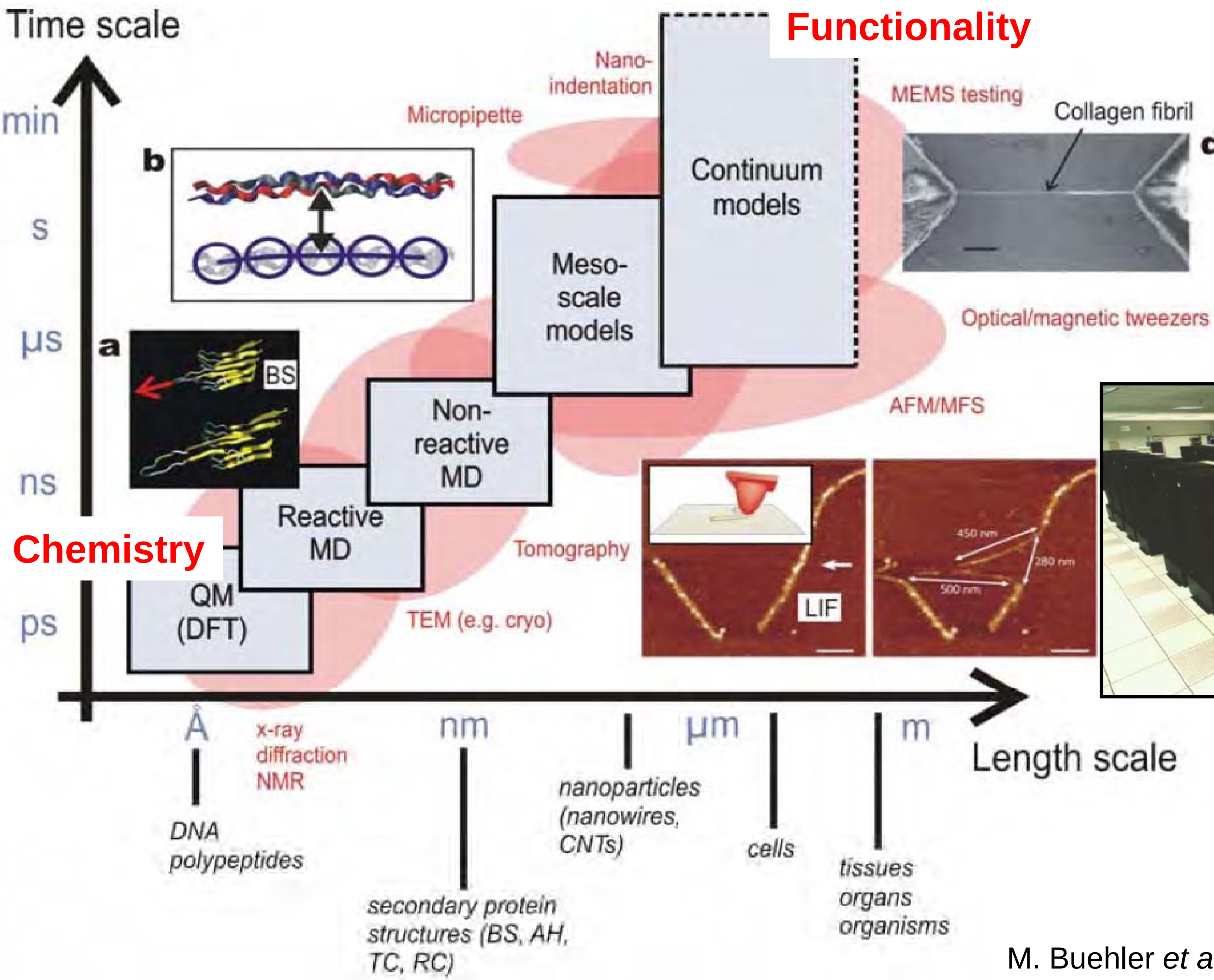
covalent bonds ***electrostatic bonds*** ***weak bonds***





M. Buehler, *Atomistic Modeling of Materials Failure*, Springer, 2008

Integration with experimental techniques

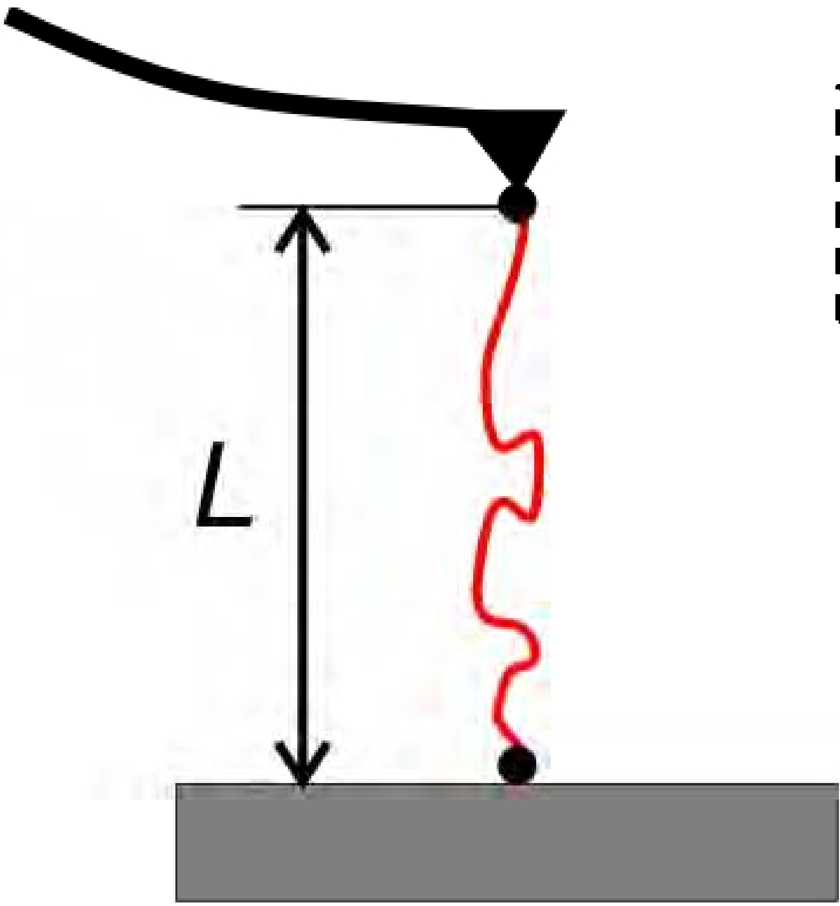


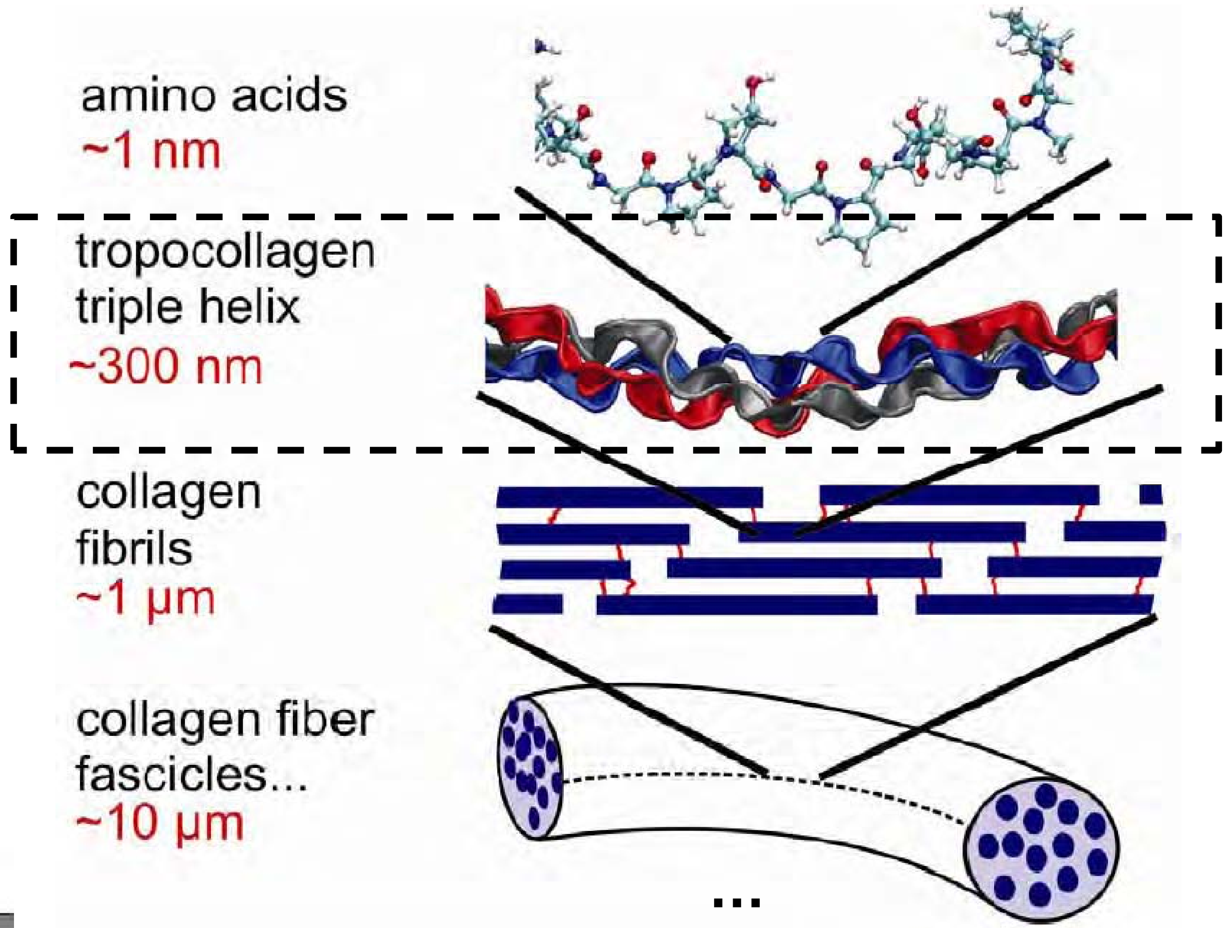
Feed parameters
Finer trains coarser

Key tool: Large-scale computing

M. Buehler *et al*., *Nature Materials*, 2009

Pulling on a single collagen molecule

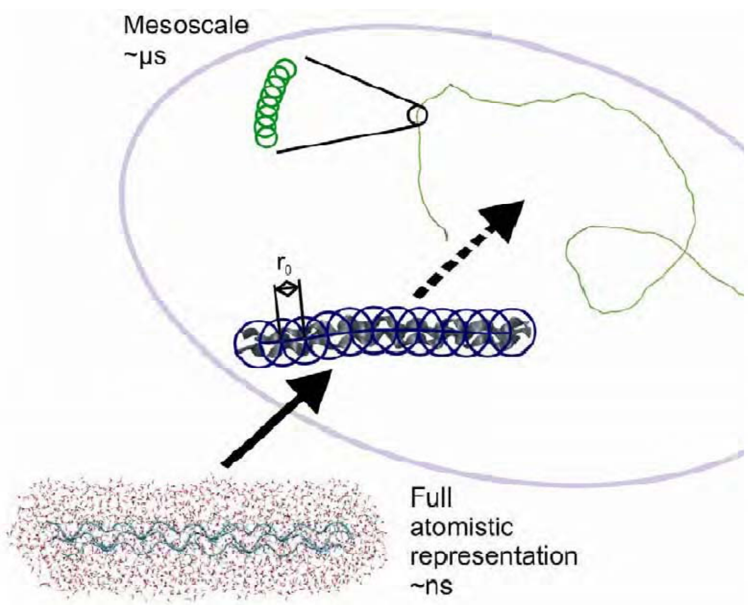




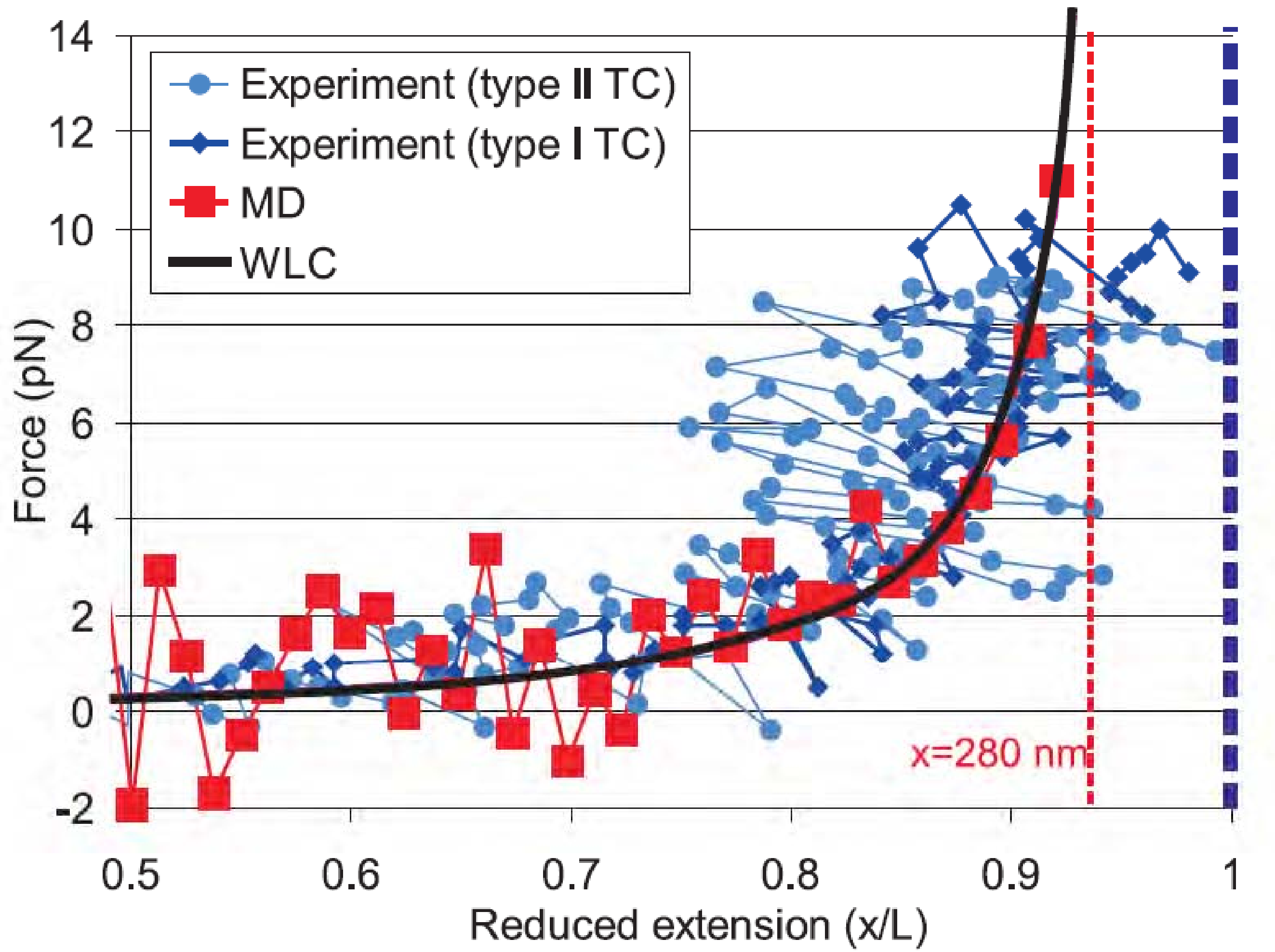
M.J. Buehler, *Proc . Nat'l Academy of Sciences USA,* 2006

Pulling on a single collagen molecule

Coarse-graining



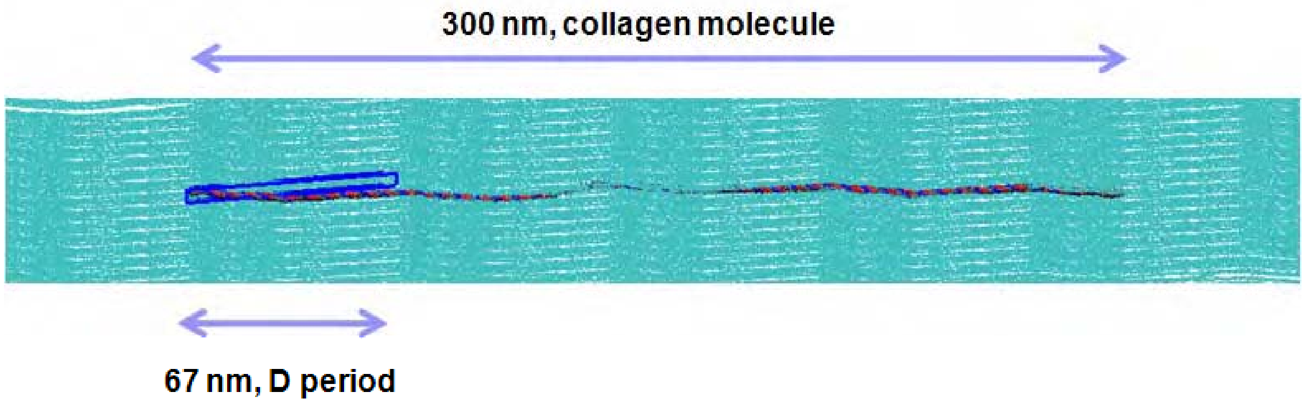
Mechanism:
Entropic elasticity
(change in configurational entropy)

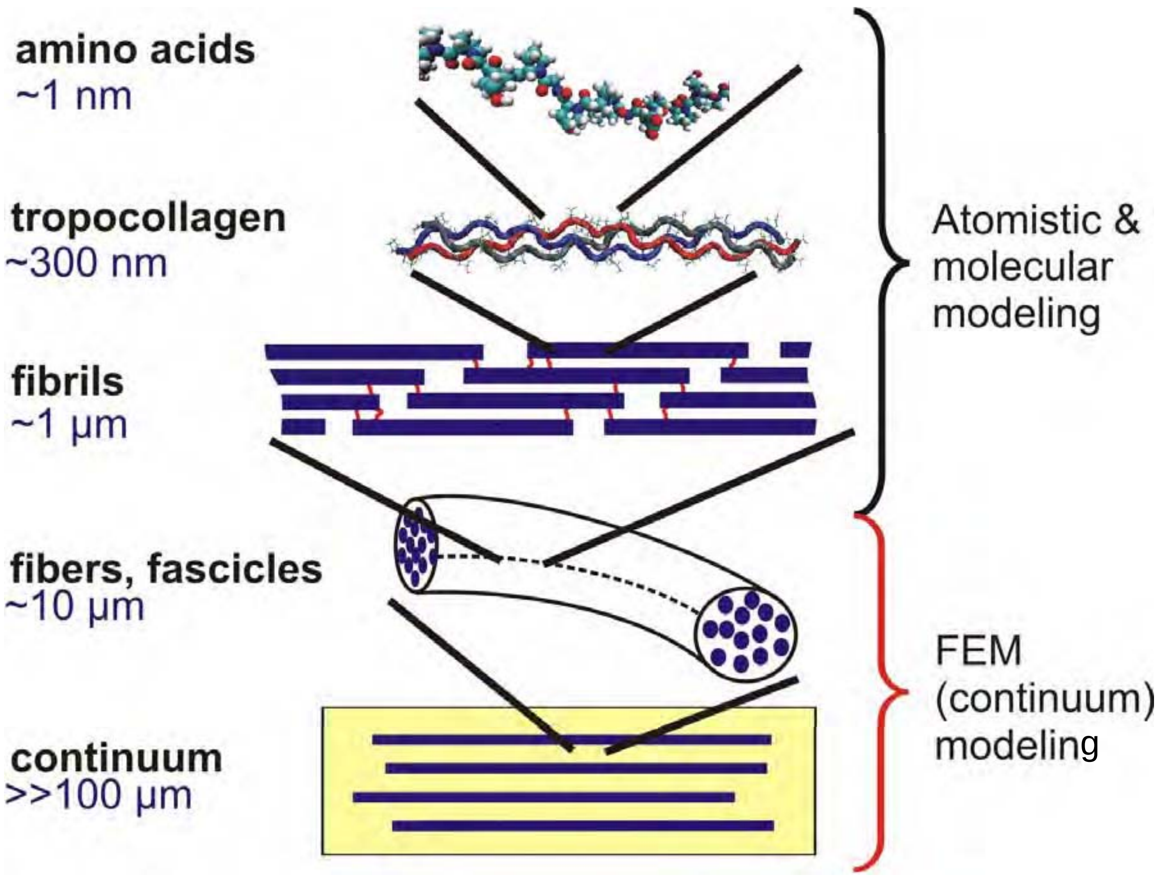


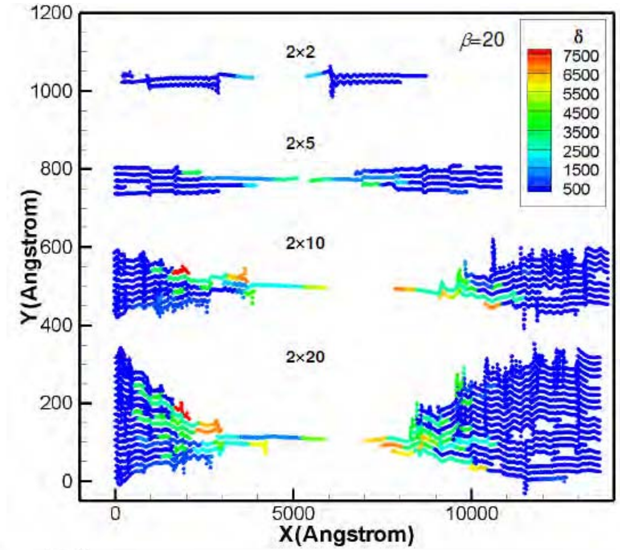
Advancement in experimental equipment:
Have quantitatively confirmed predictions from our simulations

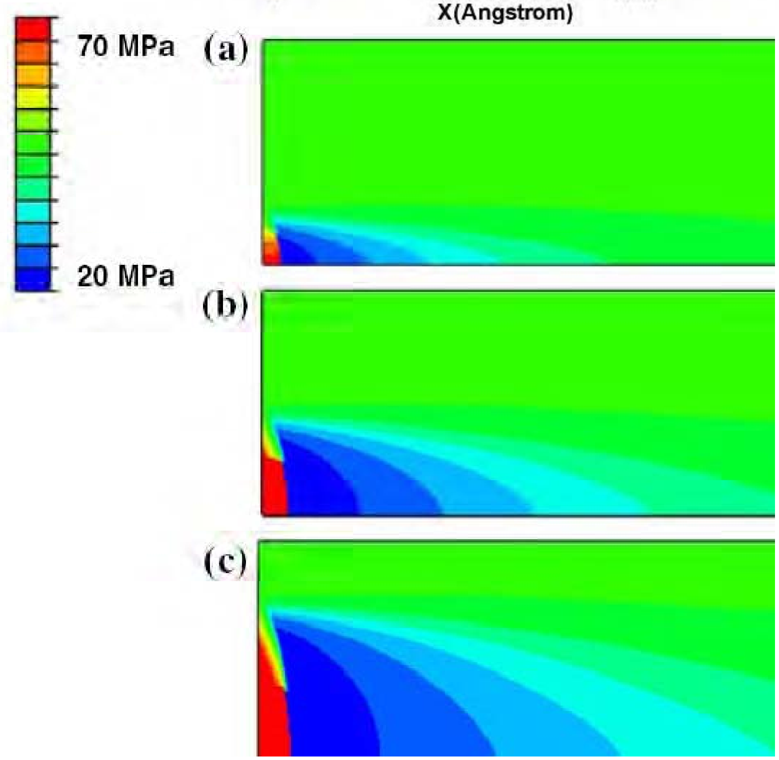
Sun *et al.*, *J. Biomechanics*, 2004; Buehler and Wong, *Biophys. J., 2007*

Hierarchical features of soft collagenous tissue





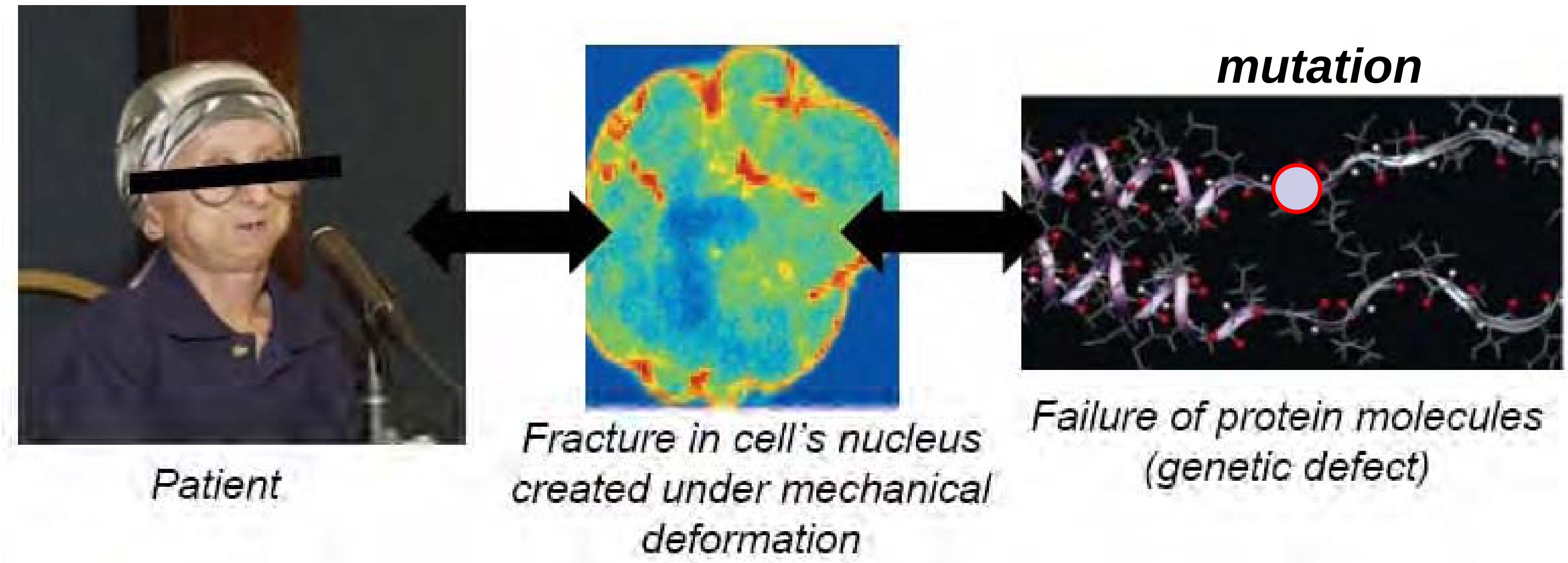




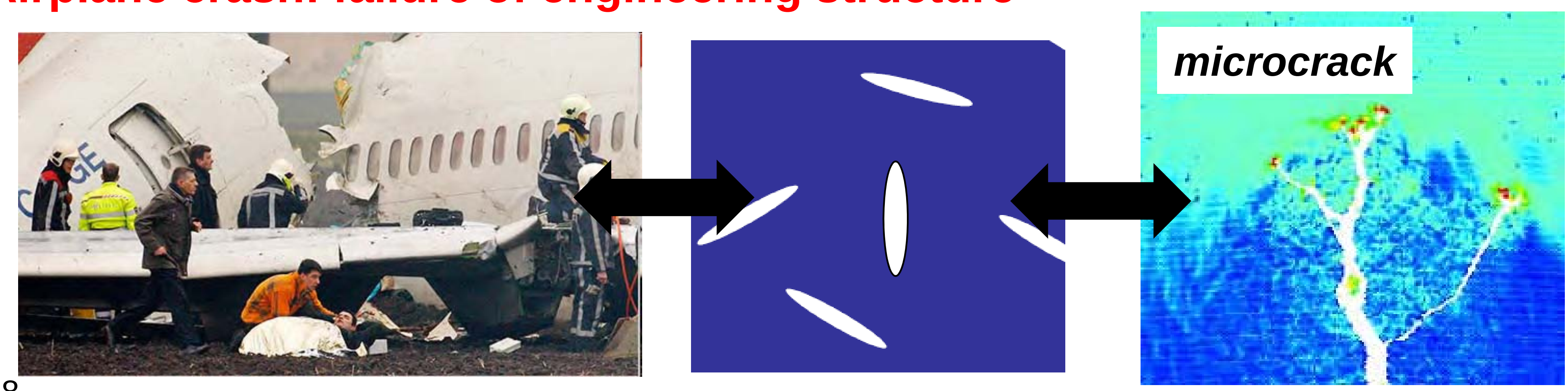
B. Moran, M. Buehler *et al., Annals in Biomedical Engineering,* 2009

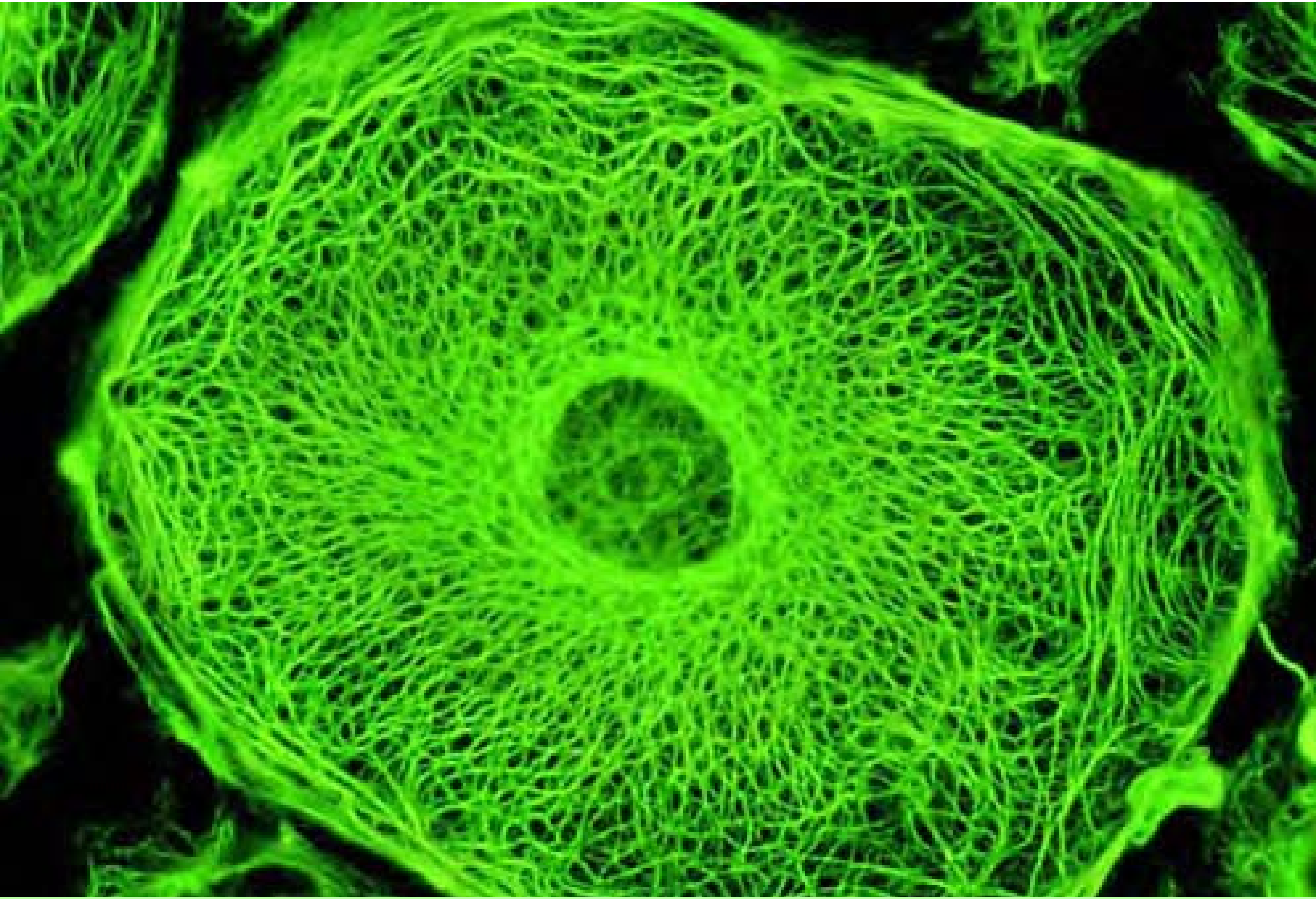
Materials failure in biology and engineering

Rapid aging disease progeria: mechanical failure of cell nucleus



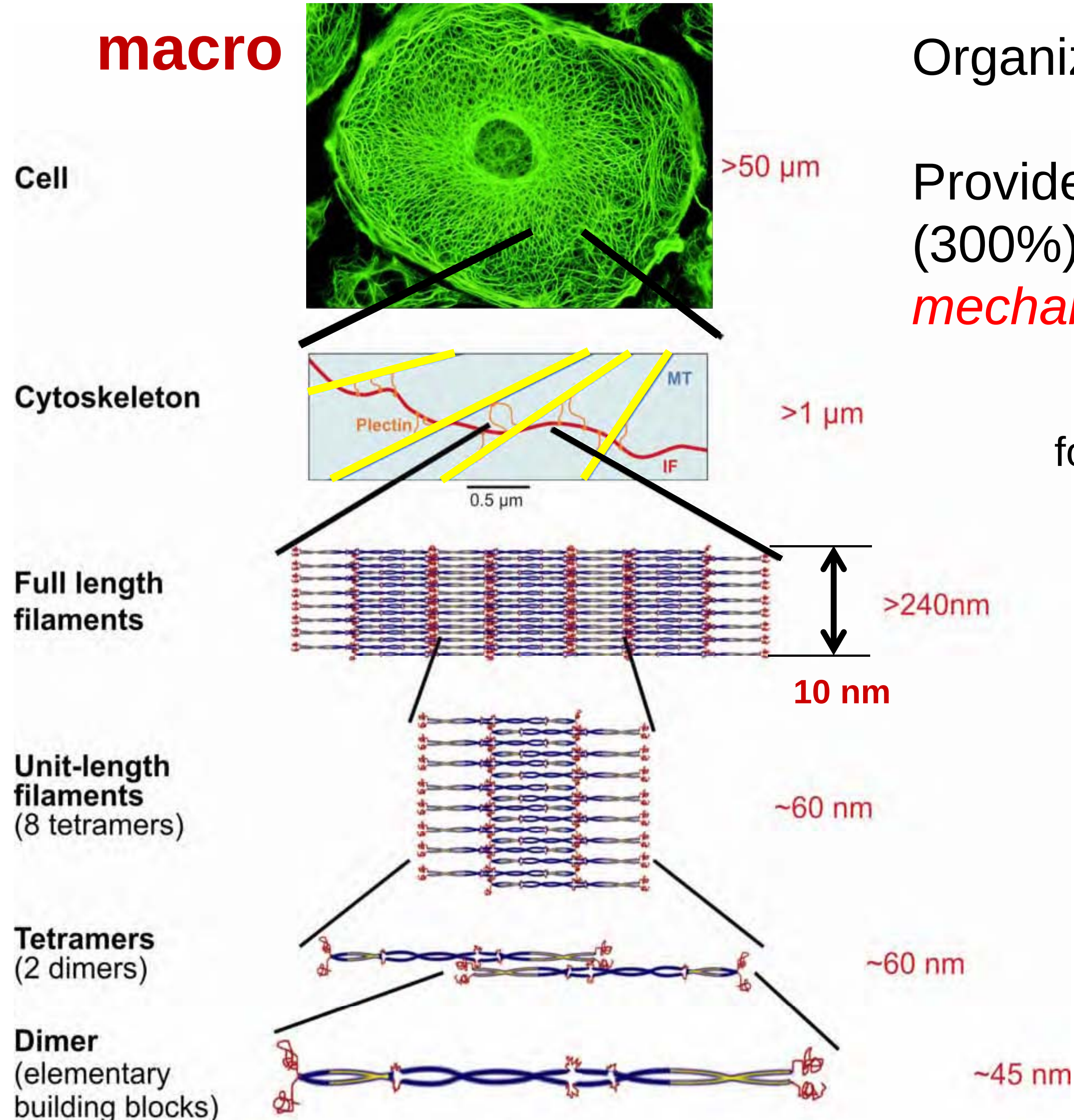
Airplane crash: failure of engineering structure





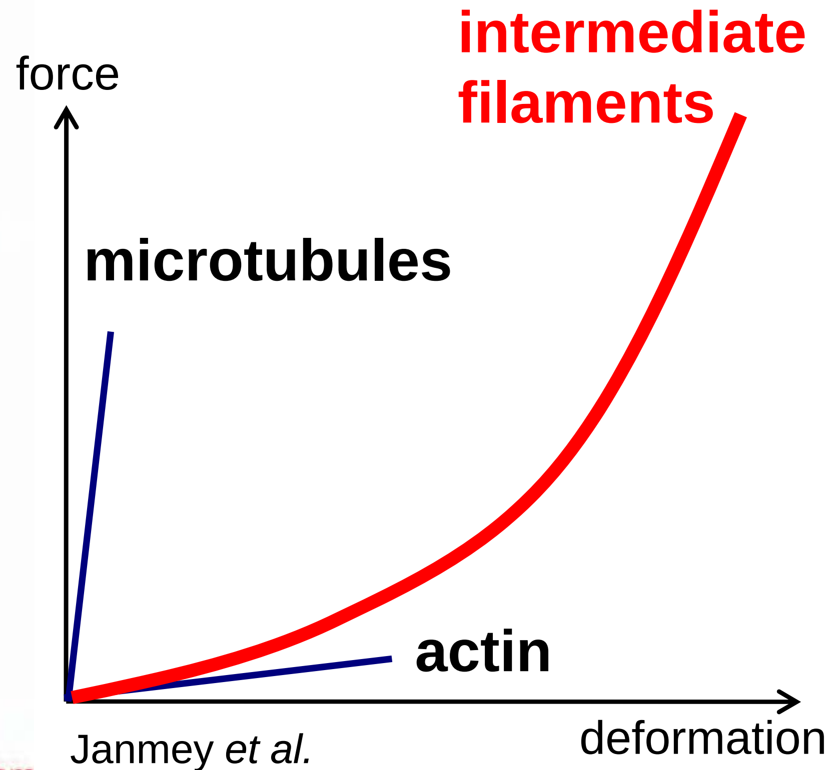
Rat kangaroo kidney epithelial - immunofluorescently labeled for keratin (intermediate filament)

Vimentin intermediate filaments (IF)

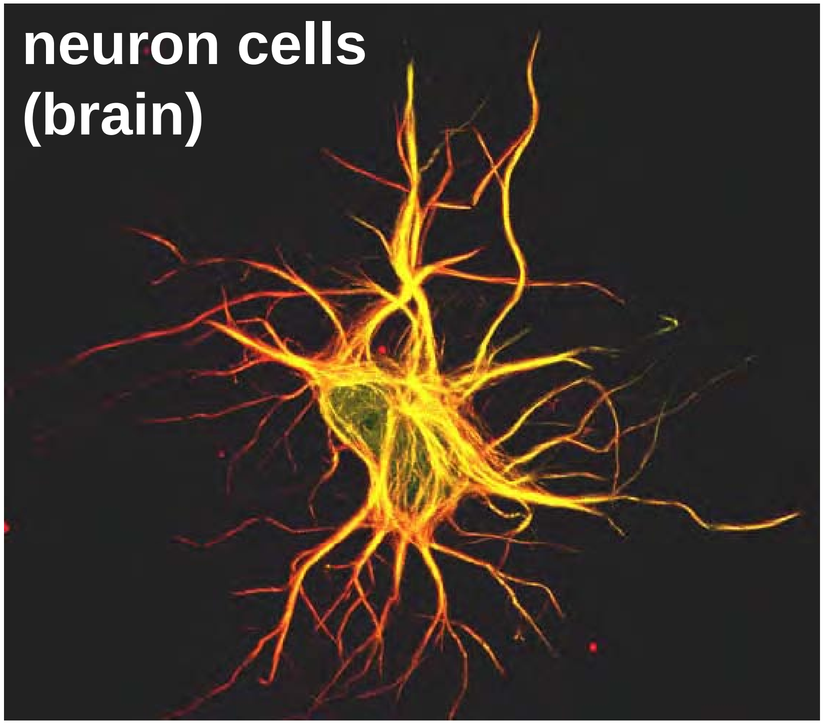


Organize the internal structure of cells

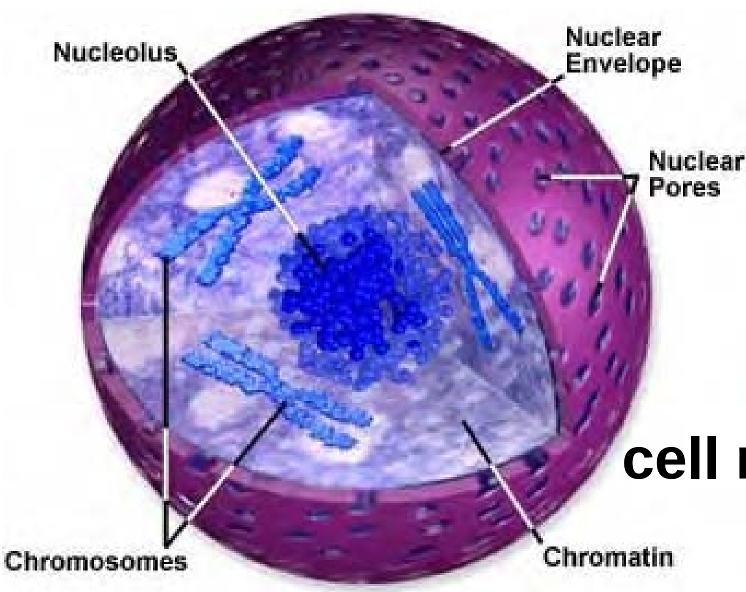
Provide strength & very extensible (300%) – *source unknown, mechanisms unknown, …*



Intermediate filaments – widely found in nature

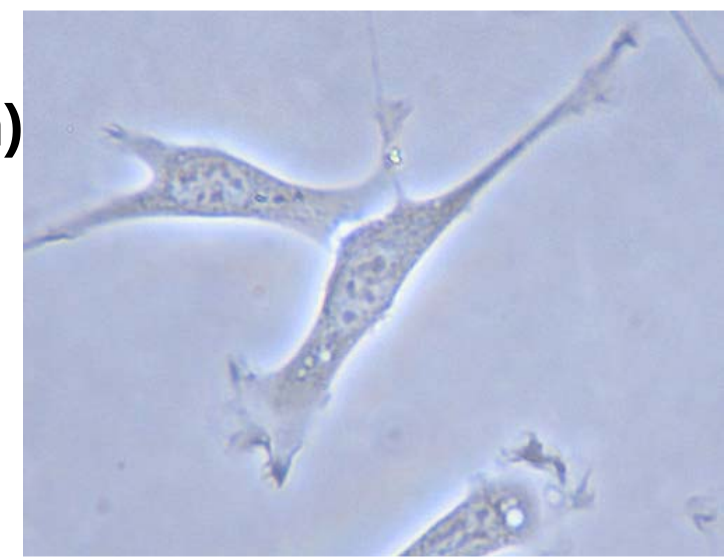


hair, hoof



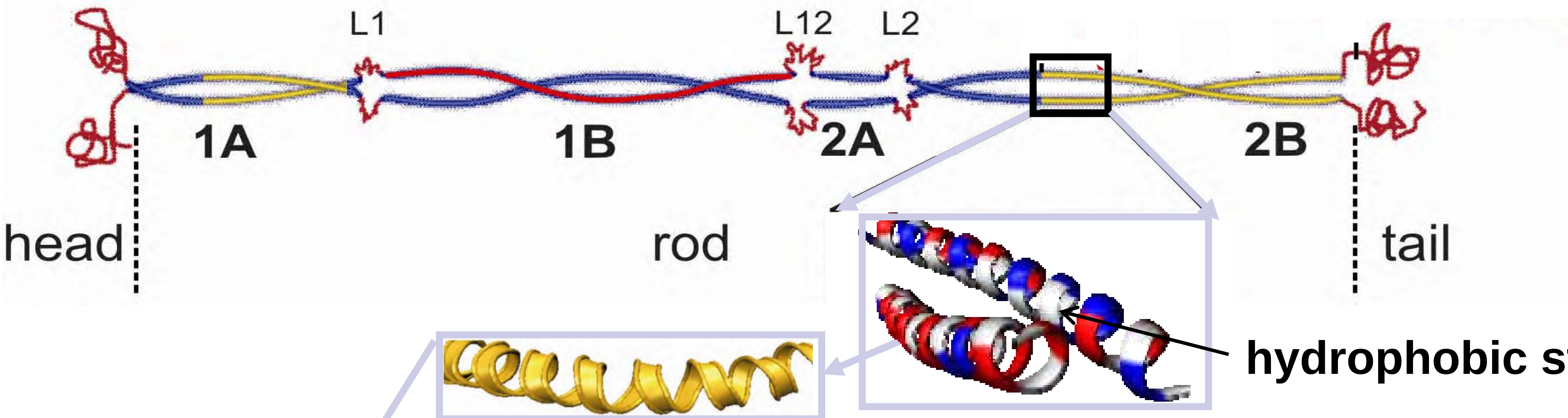
cell nucleus

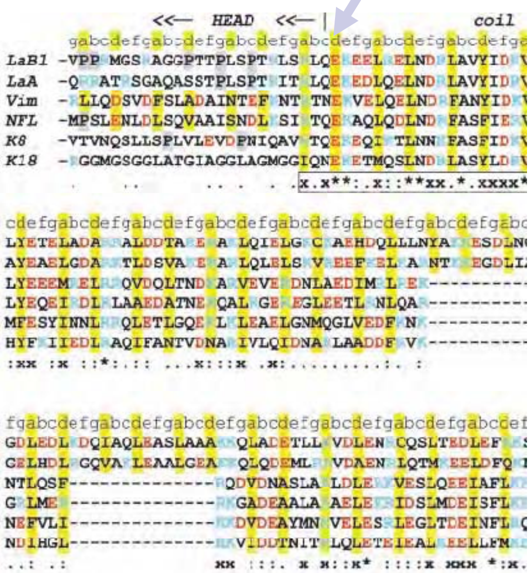
fibroblast cells (make collagen)



Intermediate filaments dimer structure

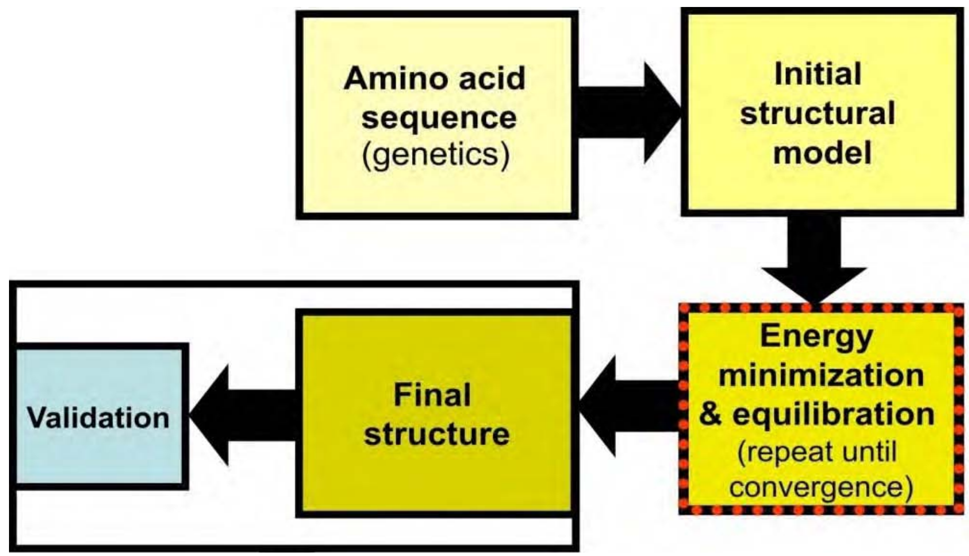
Crystallized: Part of 1A and 2B (structure not known of other parts)





$\phi = -58^\circ$

$\psi = -47^\circ$

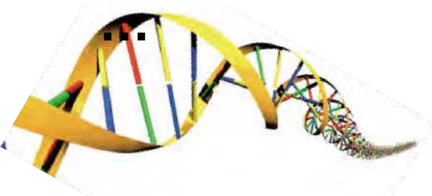


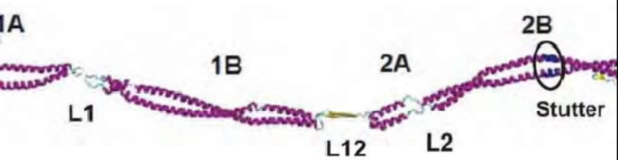
Z. Qin, L. Kreplak, M. Buehler, *PLoS ONE*, 2009

Structure prediction and functional properties

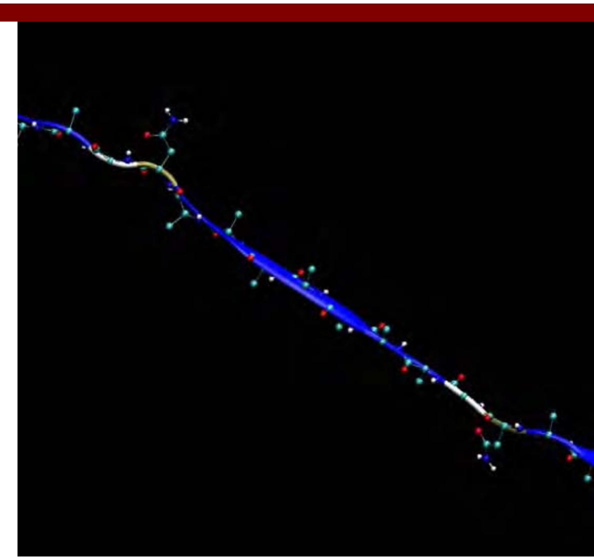
Genetics

...GGLGGQGAGA AAAAAGGAGQG

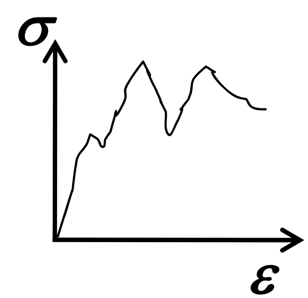




Amino acid sequence → **Replica Exchange Simulations** → **Ensemble of final structures** → **Validation (experimental results)** → **Mechanical characterization (multiscale)**



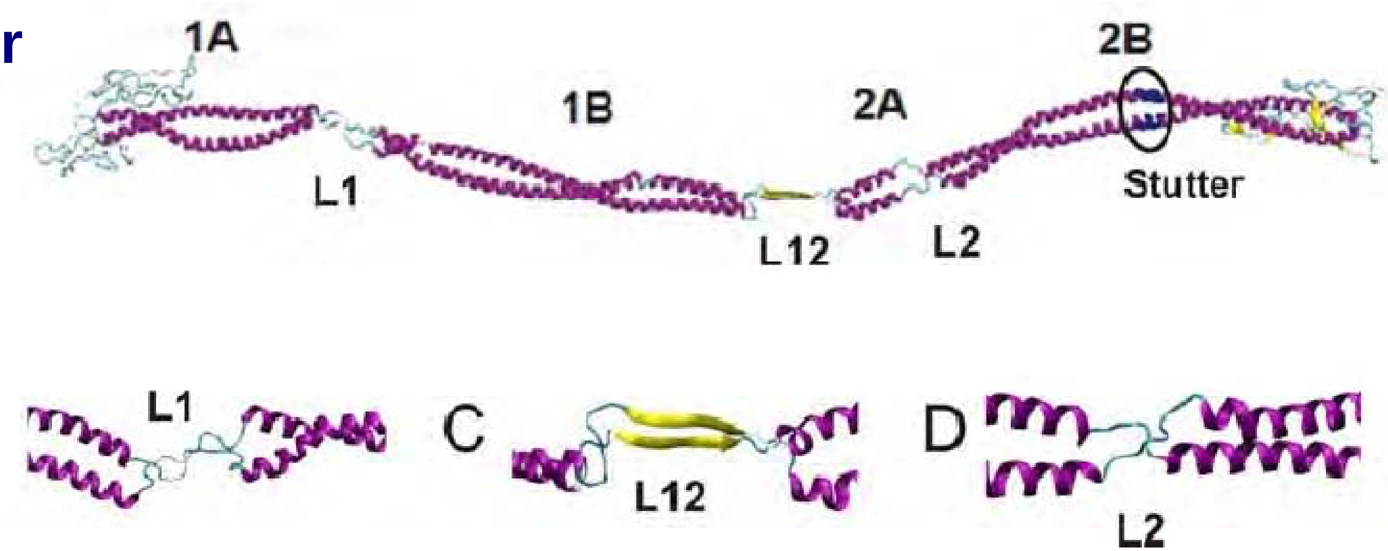
Structure



Mechanics (functionality)

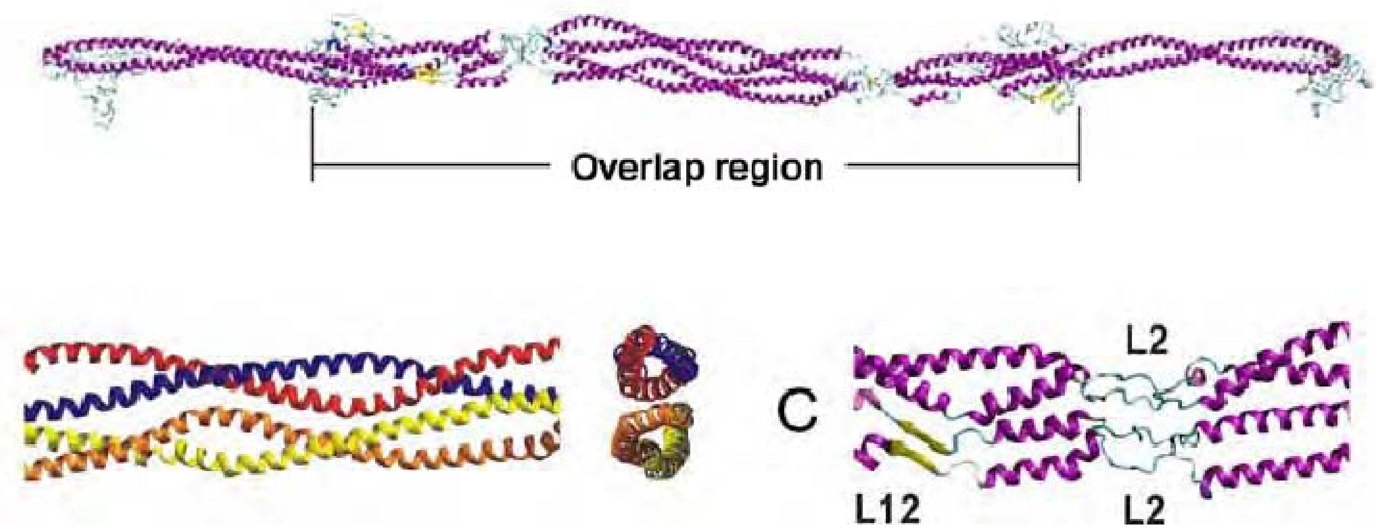
Molecular structure of the dimer and tetramer

Dimer



Linker domains provide flexible "hinges"

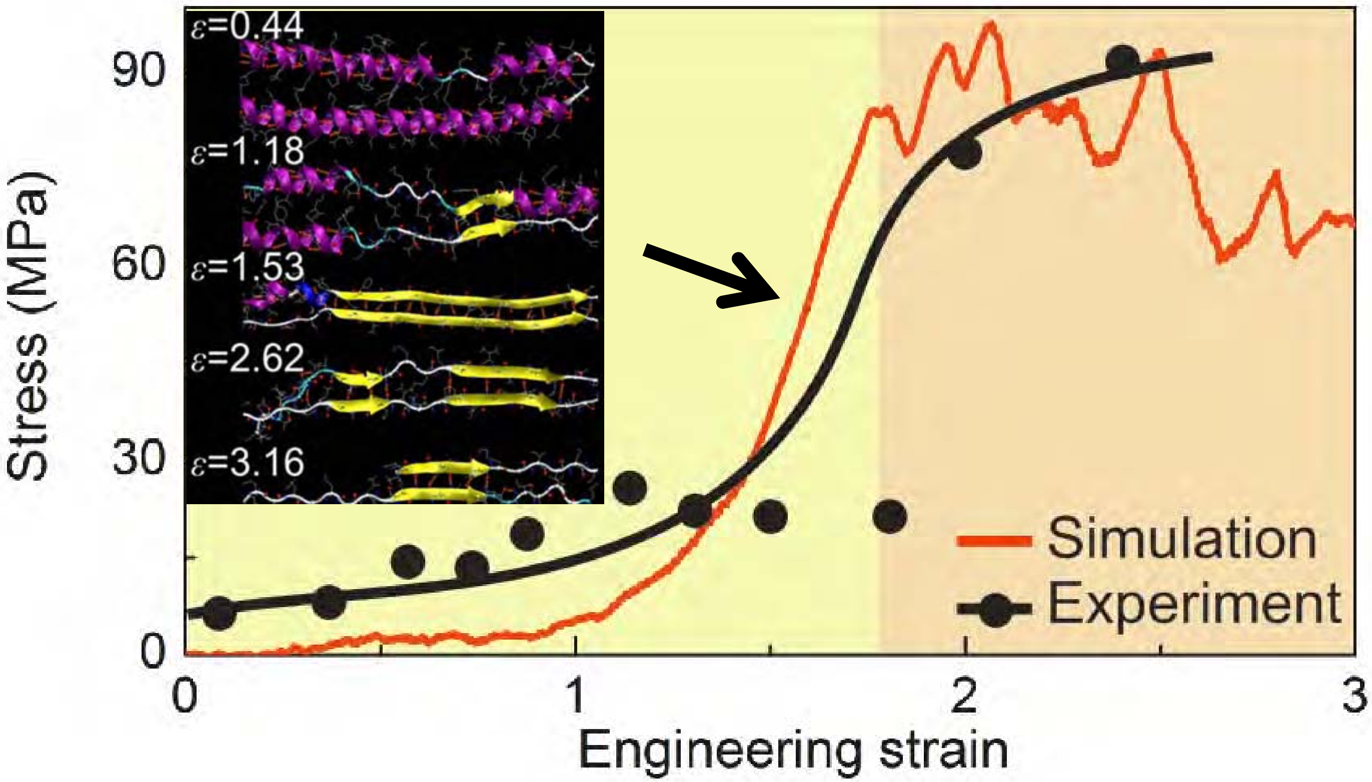
Tetramer



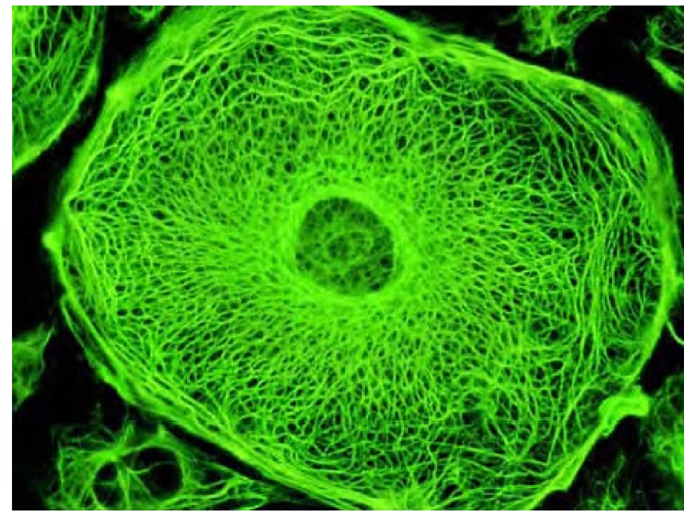
Linker L2 provides assembly template

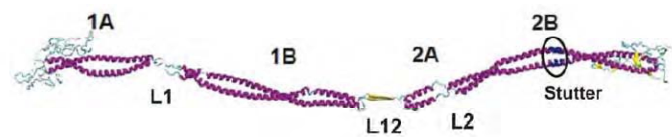
Z. Qin, L. Kreplak, M. Buehler, *Nanotechnology,* 2009; *PLoS ONE*, 2009

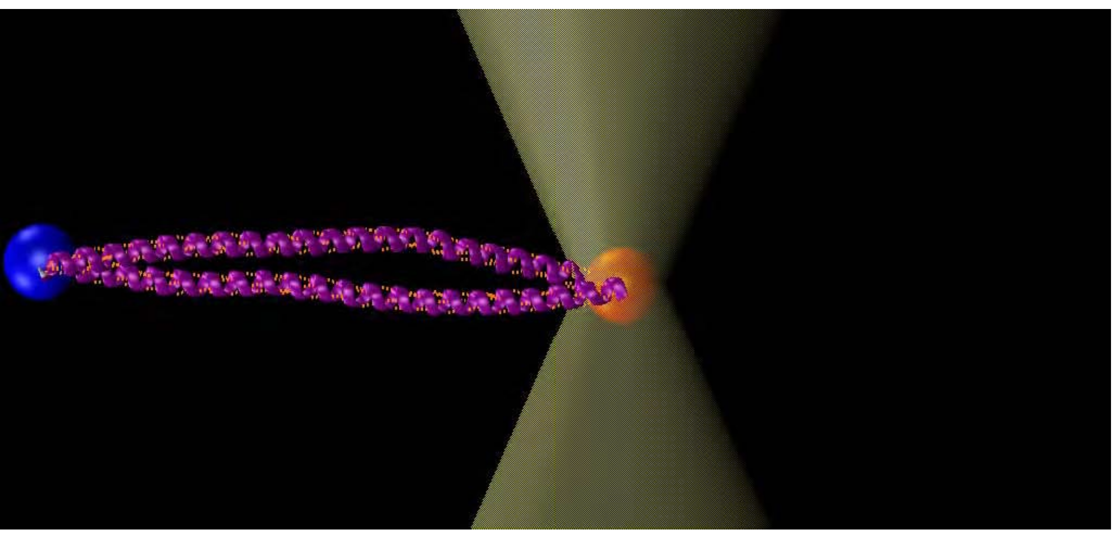
Stretching of intermediate filament protein

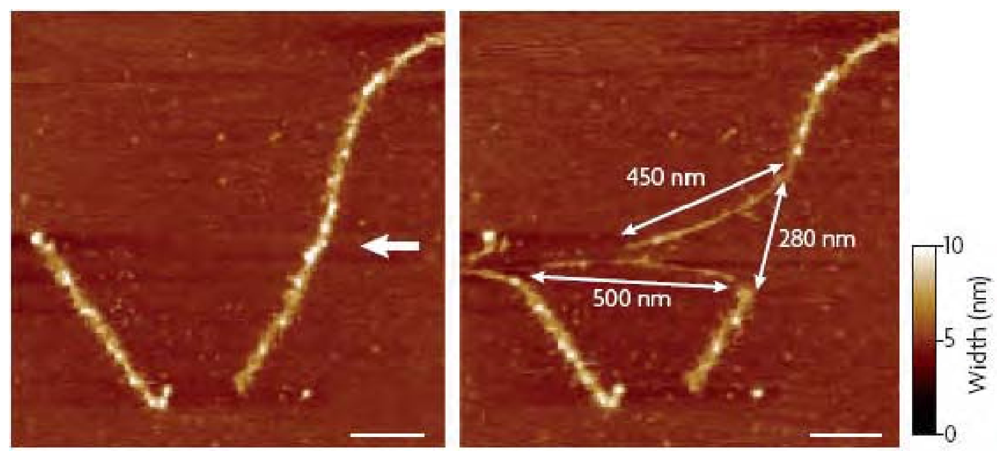


Z. Qin, L. Kreplak, M. Buehler,
PLoS ONE, 2009; *PRL*, 2010

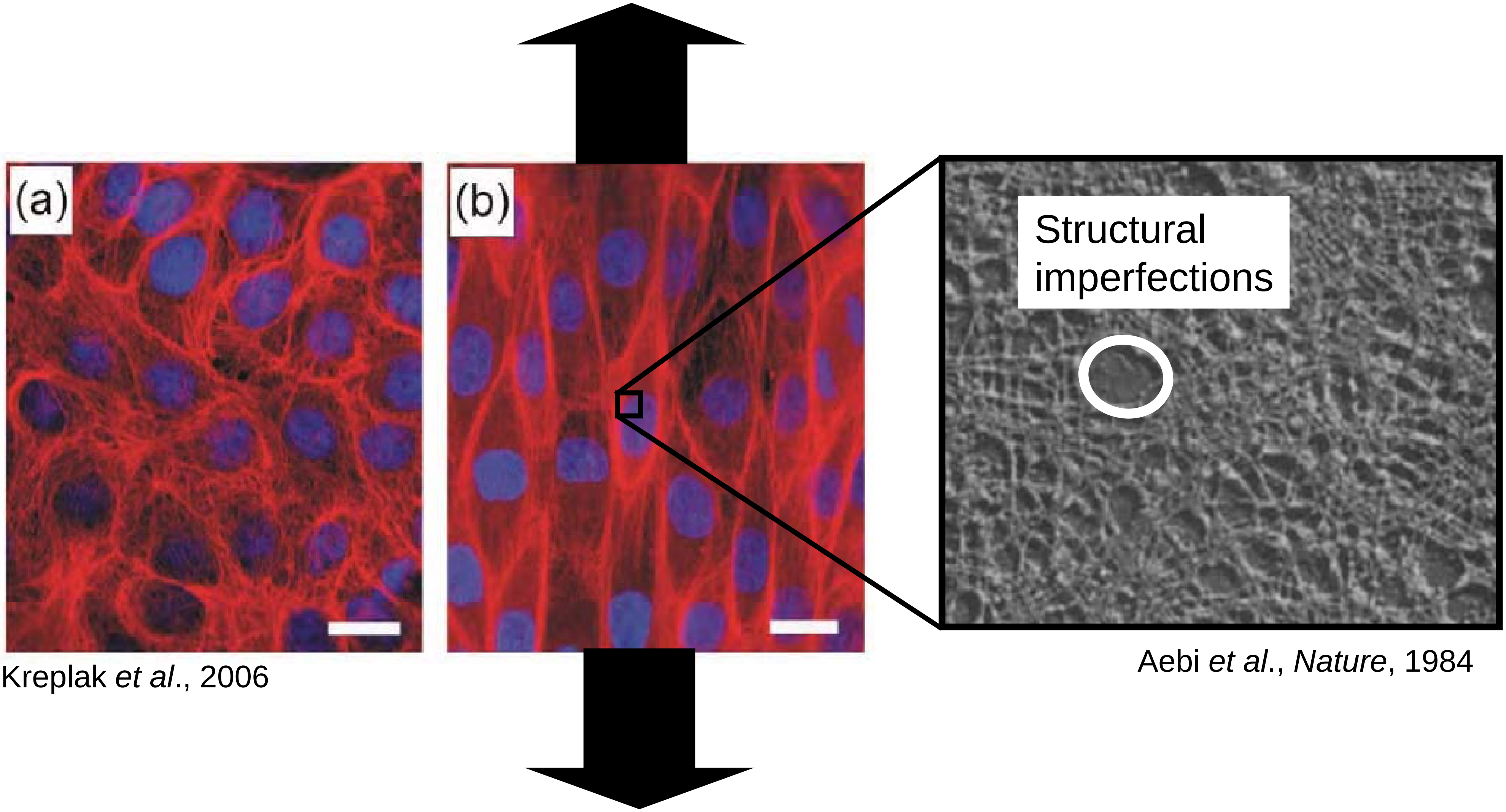








Larger-scale protein network properties

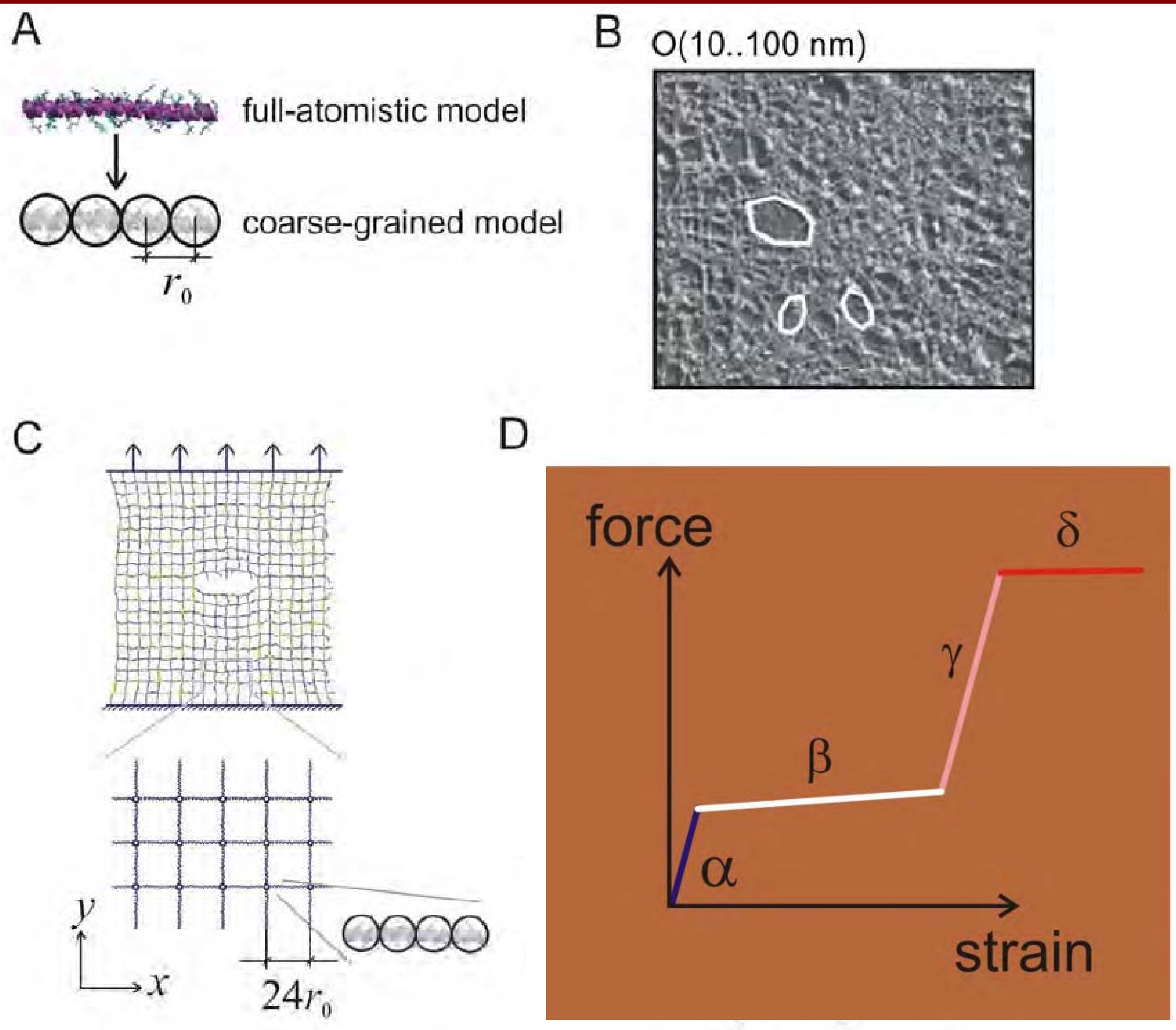


Kreplak *et al*., 2006

Aebi *et al*., *Nature*, 1984

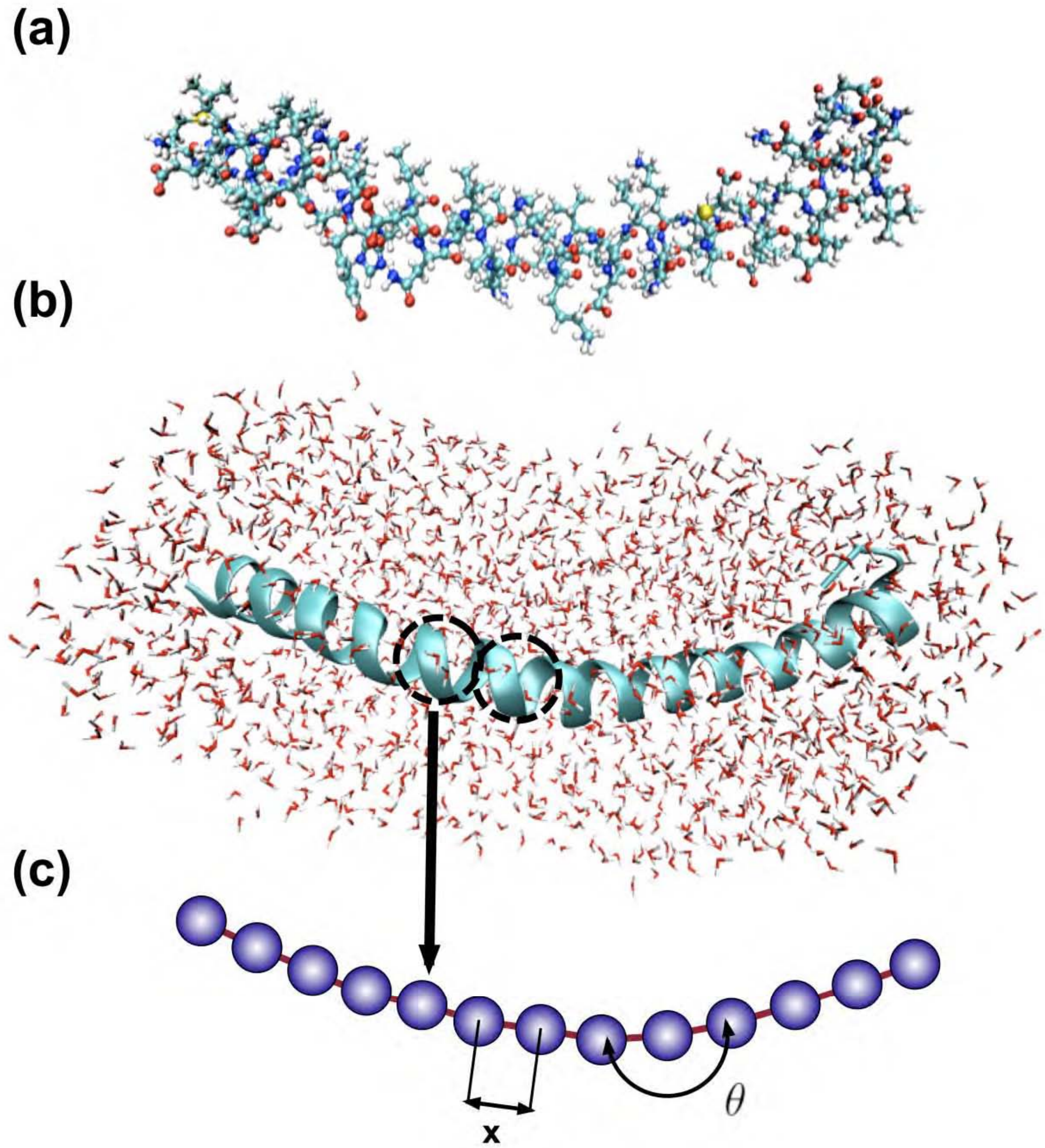
How does behavior of protein network at larger scale depend on the protein constituent's structure?

Lamin intermediate filament network (cell nucleus)



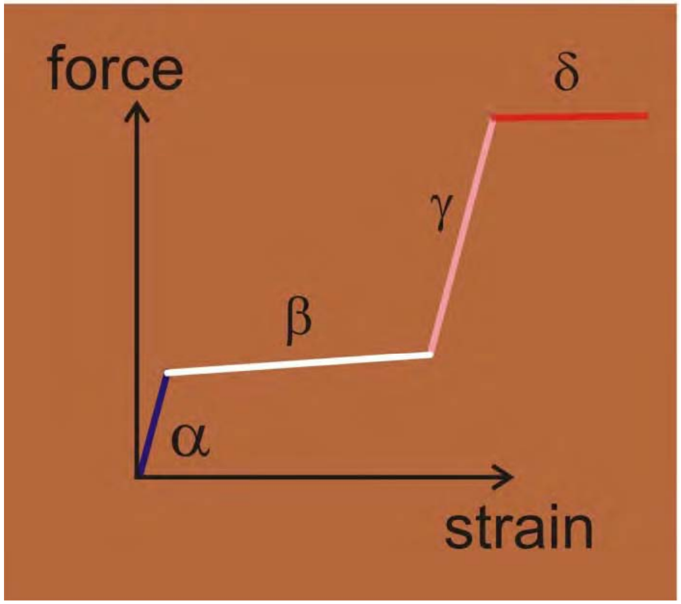
Ackbarow *et al., PNAS*, 2007; Ackbarow, Buehler *et al*., *PLoS ONE*, 2009

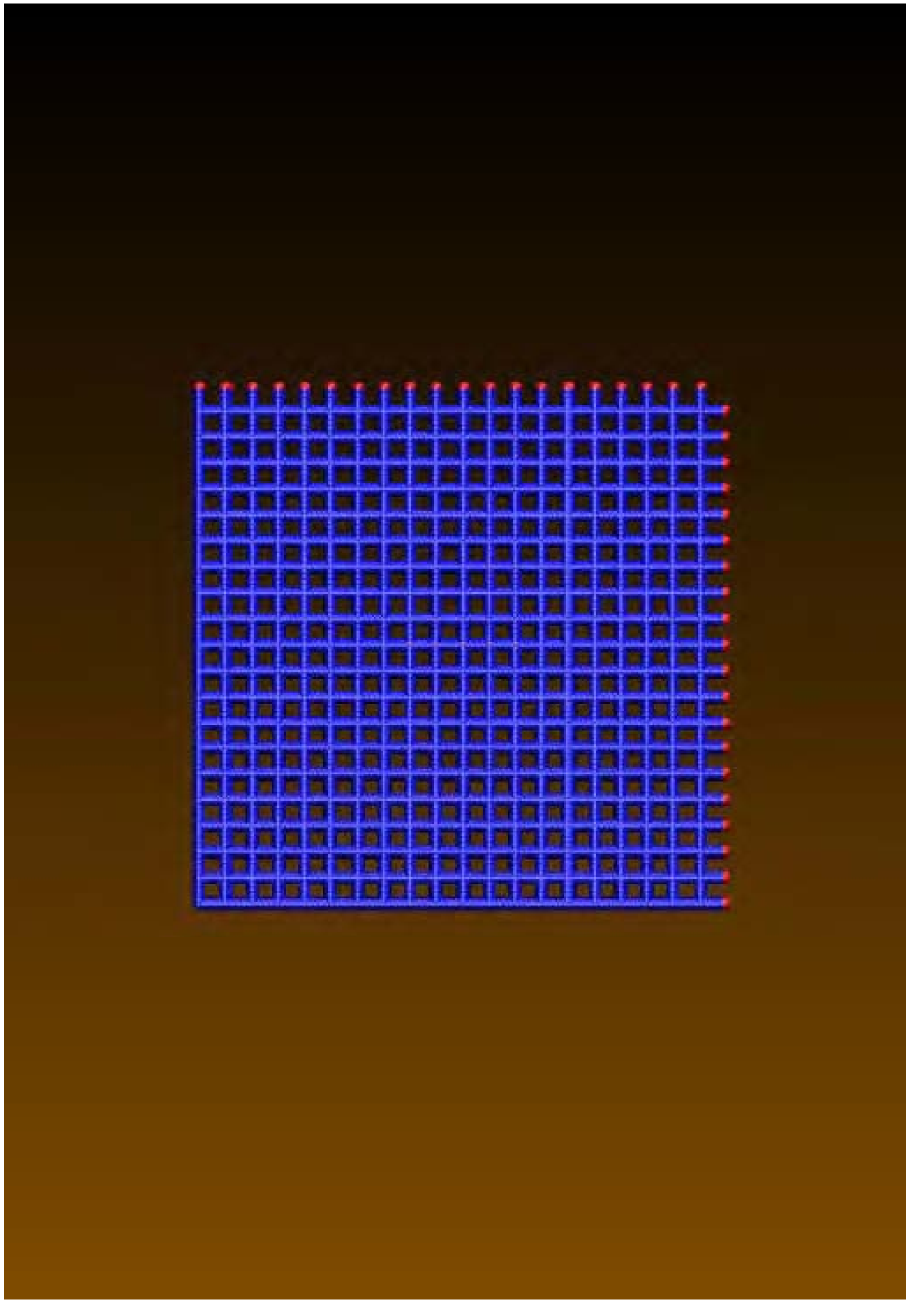
Coarse-graining approach



Movie of deformation

Intermediate filament

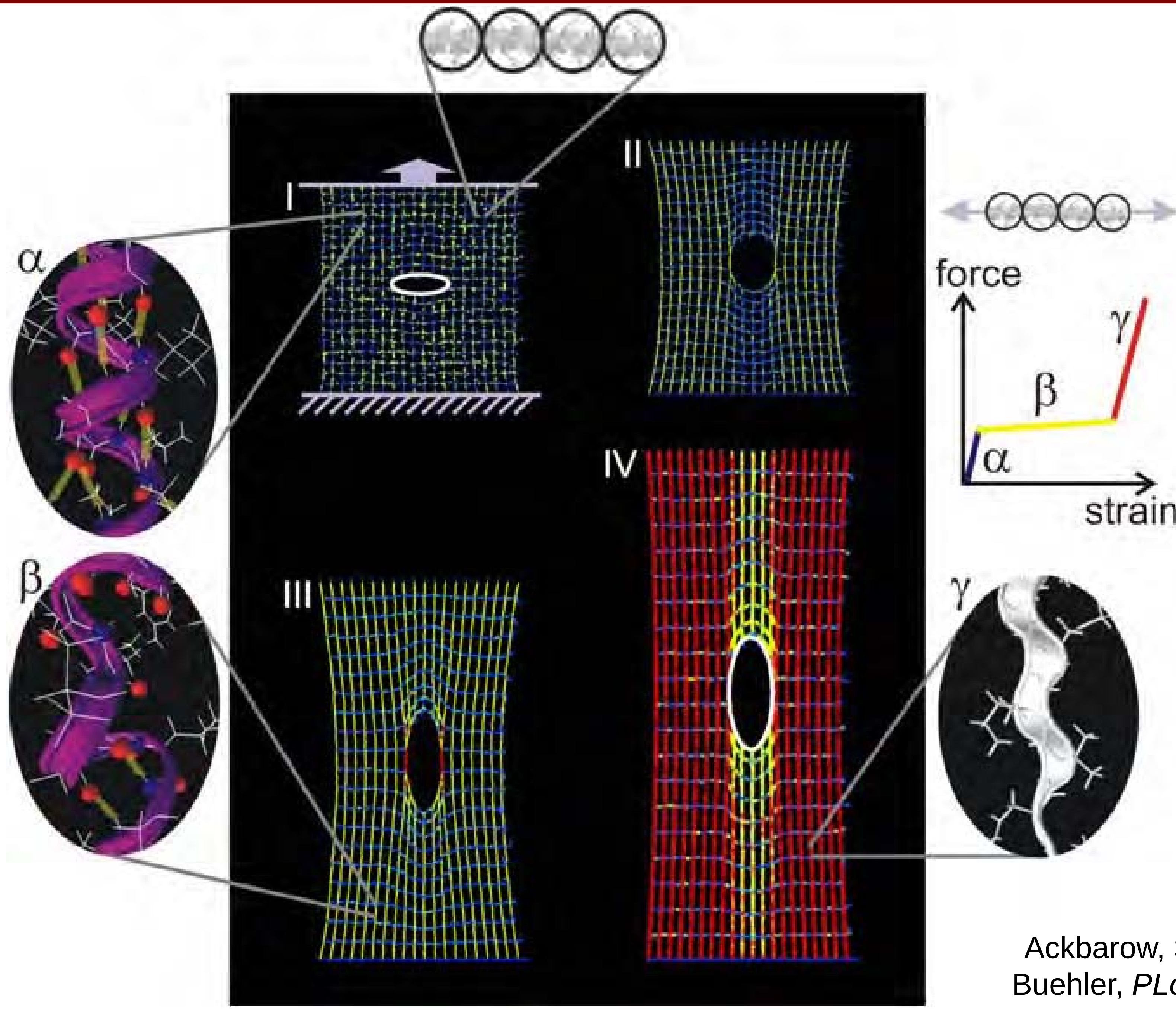




http://web.mit.edu/mbuehler/www/slides/HG-ASME/movie_filament.mpg

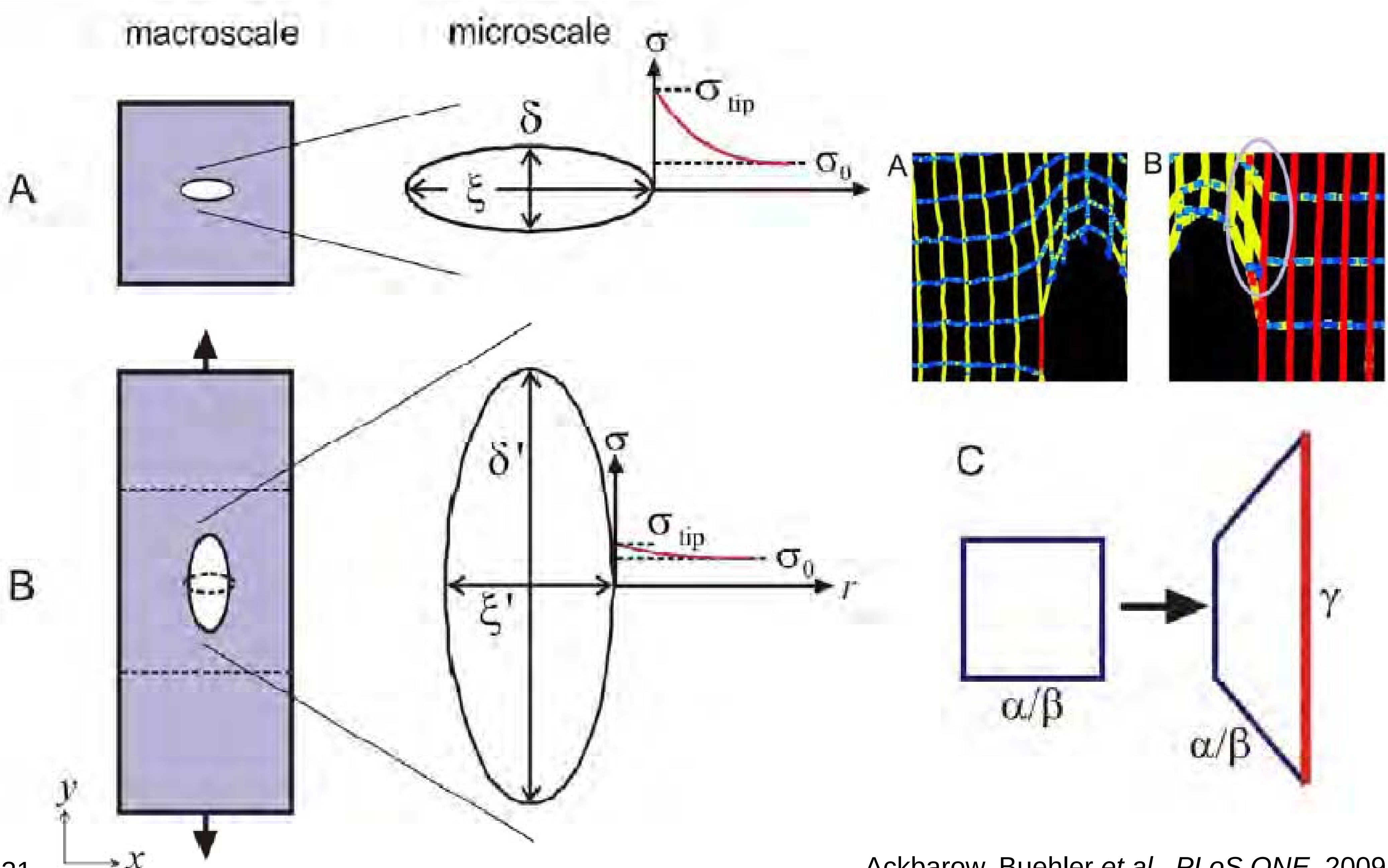
Z. Qin, L. Kreplak, M. Buehler, *PLoS ONE,* 2009;
Z. Qin et al., unpublished

Deformation behavior of alpha-helix network under strain



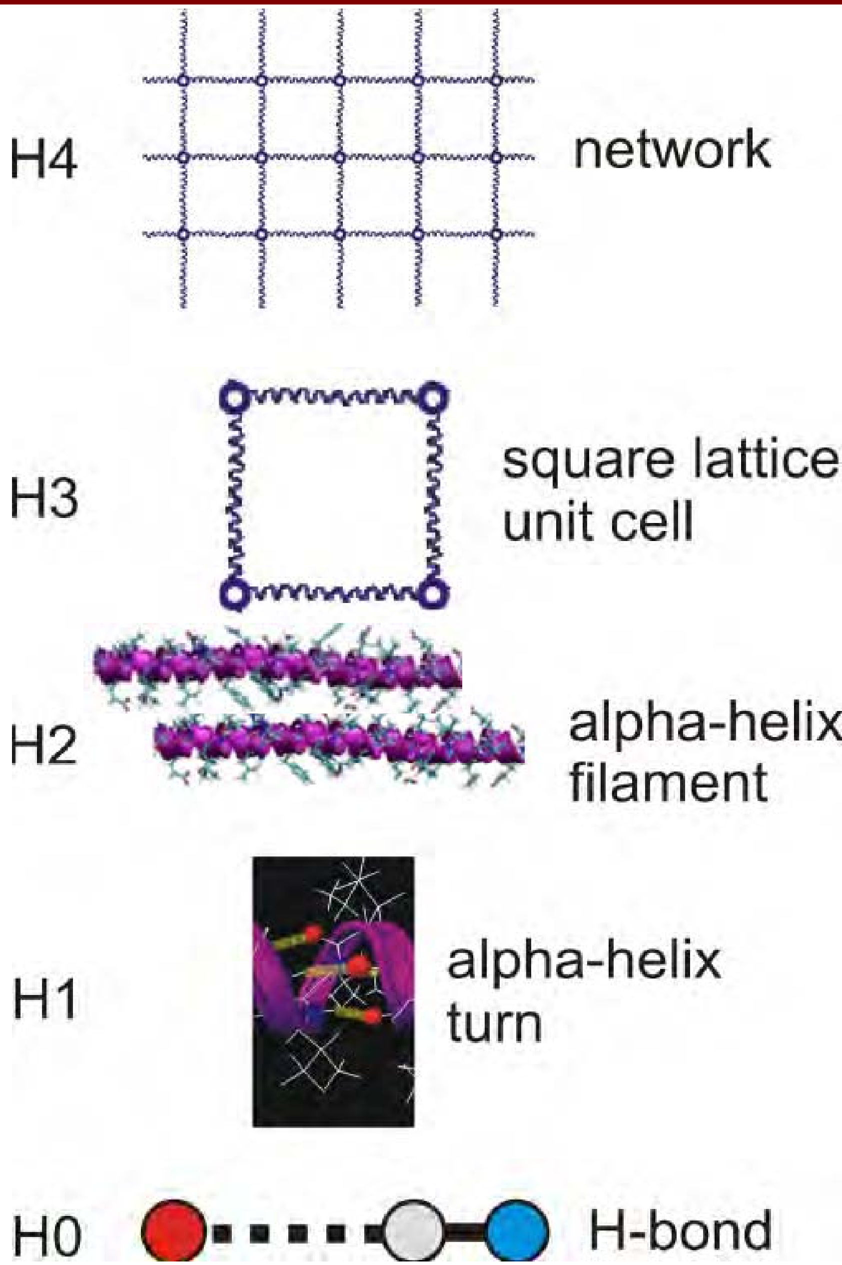
Ackbarow, Sen, Thaulow, Buehler, *PLoS ONE*, 2009

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

Directions for Basic Research in the Army

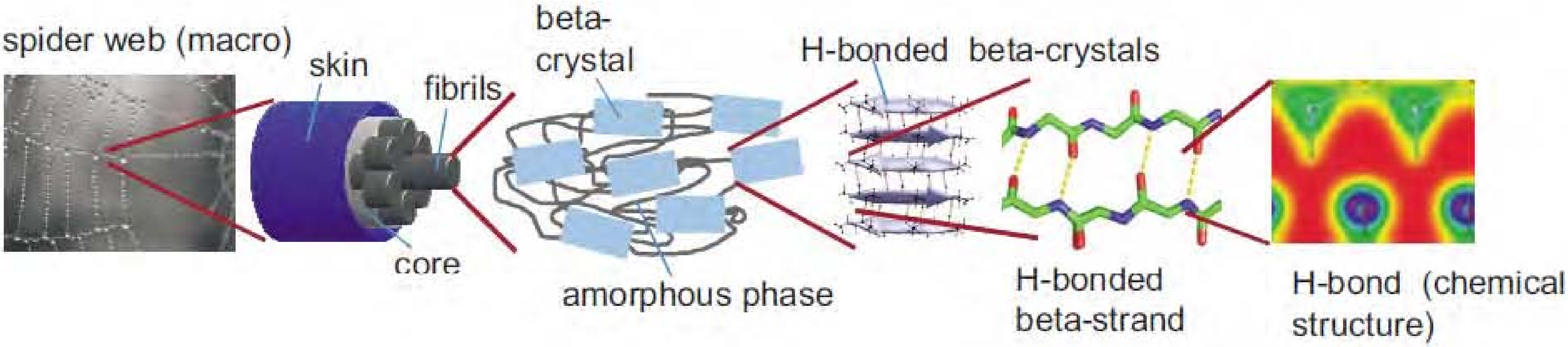
2010 Nanotechnology for Defense Conference

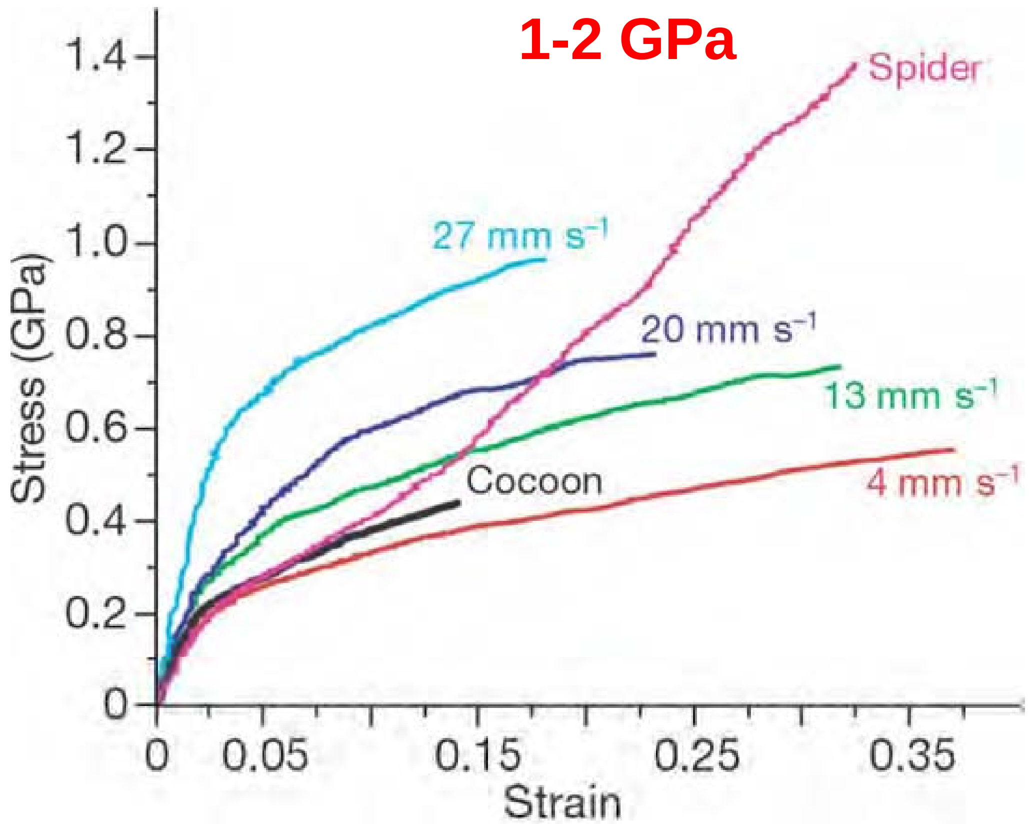
STATEMENT BY **DR. THOMAS H. KILLION**
DEPUTY ASSISTANT SECRETARY OF THE ARMY
FOR RESEARCH AND TECHNOLOGY
AND CHIEF SCIENTIST
BEFORE THE SUBCOMMITTEE ON TERRORISM,
UNCONVENTIONAL THREATS AND CAPABILITIES
COMMITTEE ON ARMED SERVICES
UNITED STATES HOUSE OF REPRESENTATIVES
ON
THE UNITED STATES ARMY'S SCIENCE AND
TECHNOLOGY (S&T)
PROGRAM FOR FISCAL YEAR 2011
SECOND SESSION, 111TH CONGRESS
MARCH 23, 2010

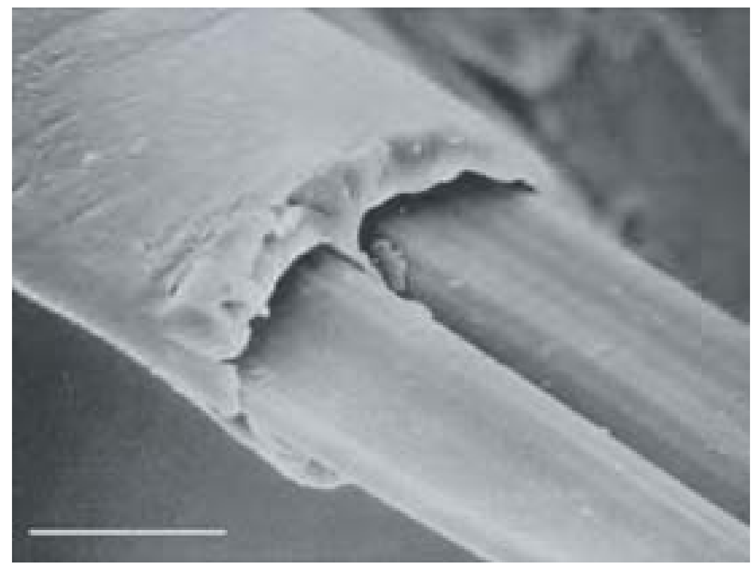
Courtesy J. Andzelm (ARL)

I will highlight of 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





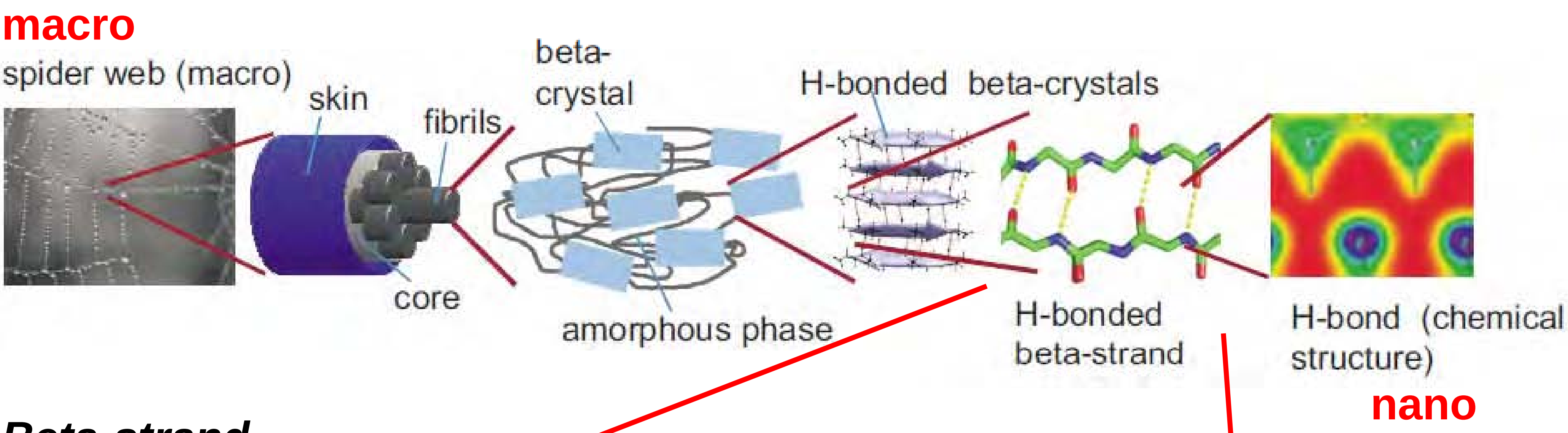


Z. Shao and F. Vollrath, *Nature*, 2002

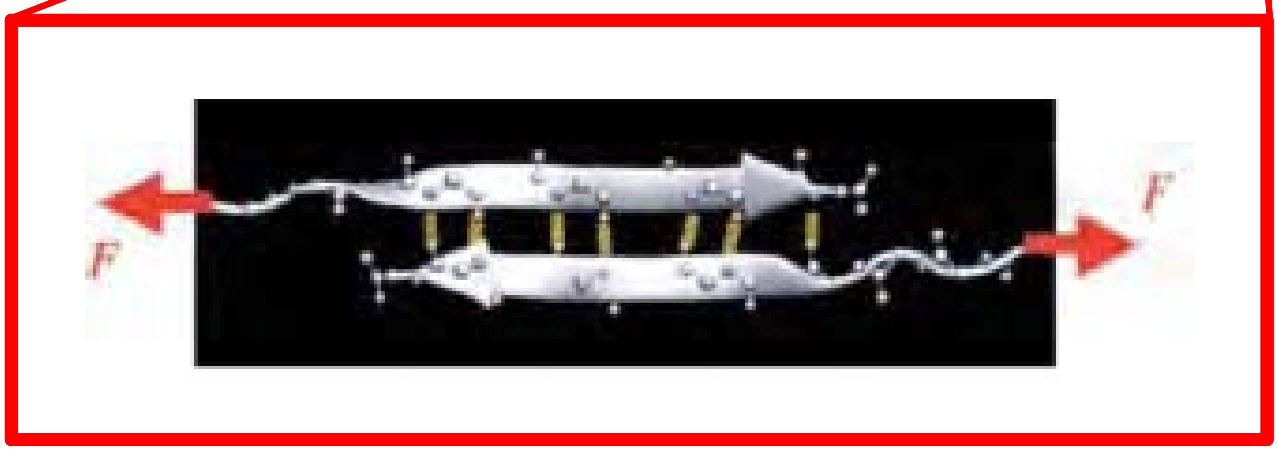
Spider silk with diameter of *O*(inch) can stop large aircraft in flight

Keten and Buehler, *Nano Letters,* 2008, Buehler *et al., Prog. Mat. Science,* 2008

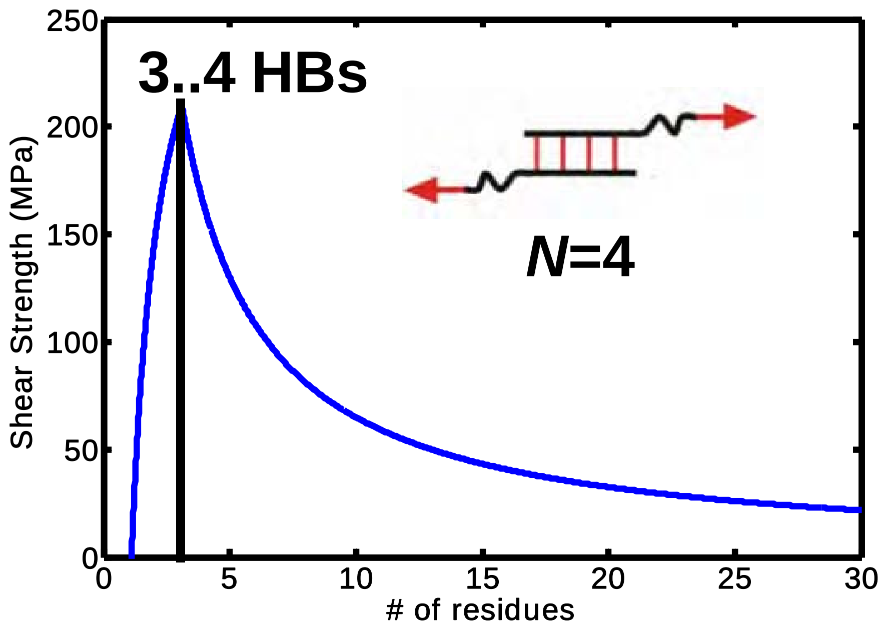
Spider silk's hierarchical structure



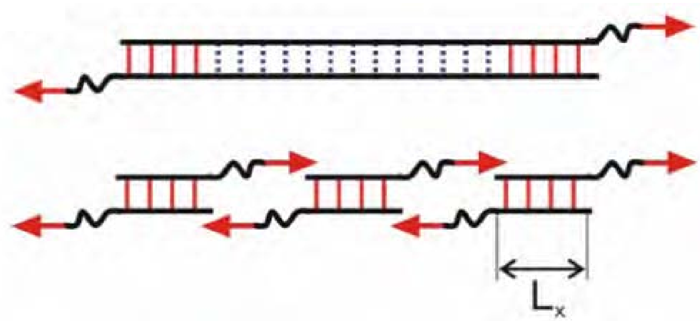
Beta-strand protein motif



Scaling of strength of H-bond assemblies

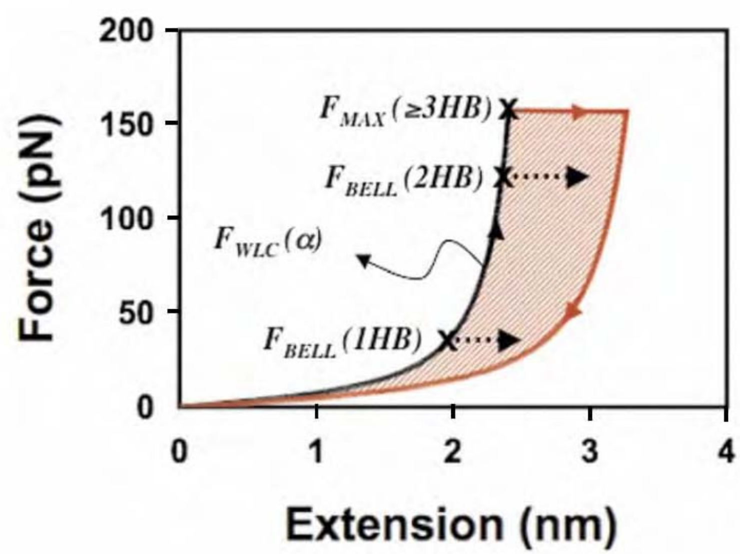


Characteristic maximum number of H-bonds work cooperatively: 3..4 H-bonds



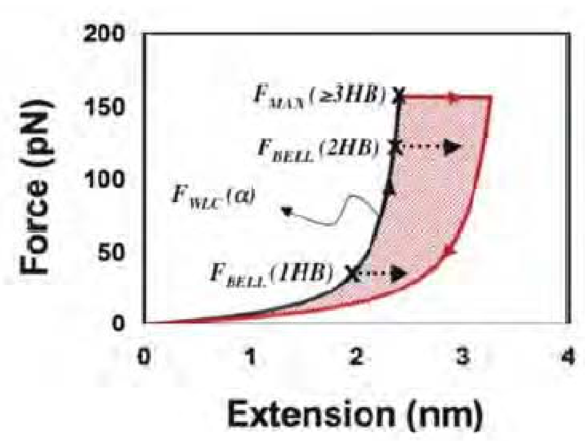
Many small segments with 3-4 HBs each enhance the strength multiple times

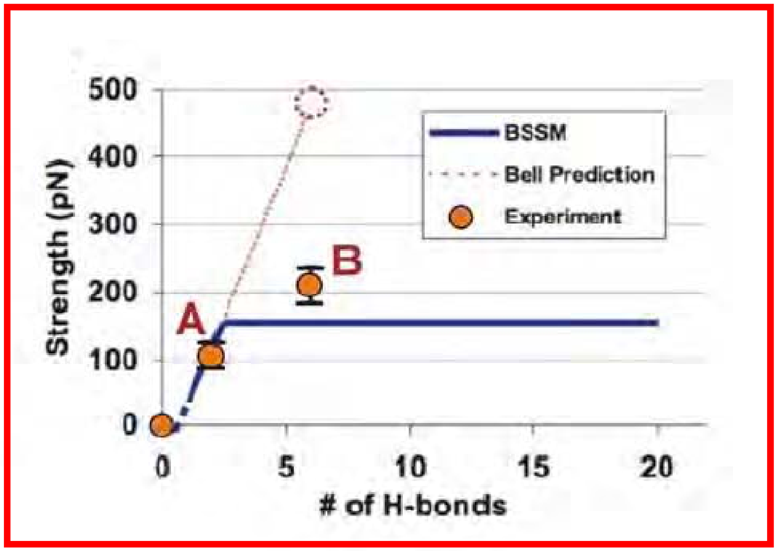
Intrinsic energetics, nanomechanics, and structural confinement control strength properties: **Reach strength at characteristic dimension of H-bond clusters**

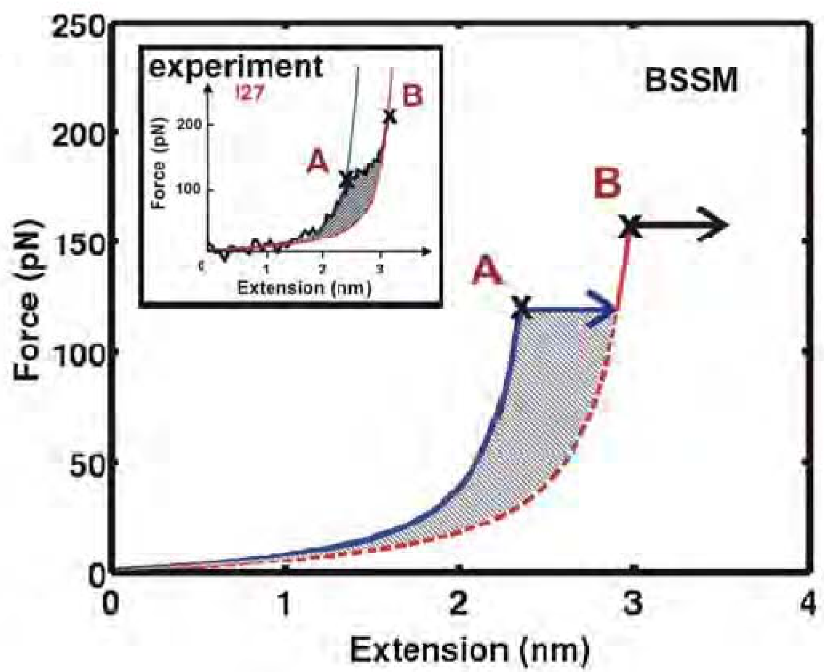


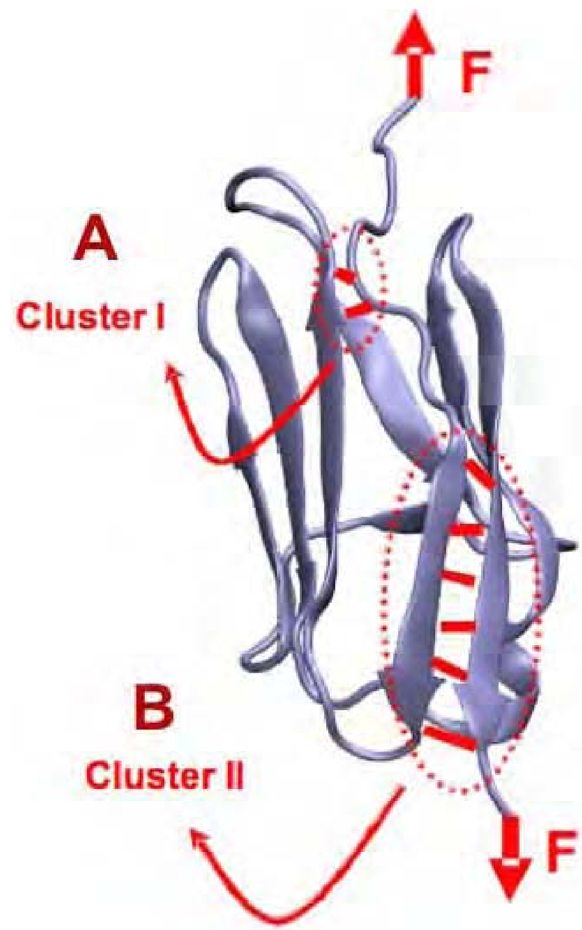
Keten and Buehler, *Nano Letters,* 2008, Buehler *et al., Prog. Mat. Science,* 2008

Size effects of strength of beta-sheet proteins





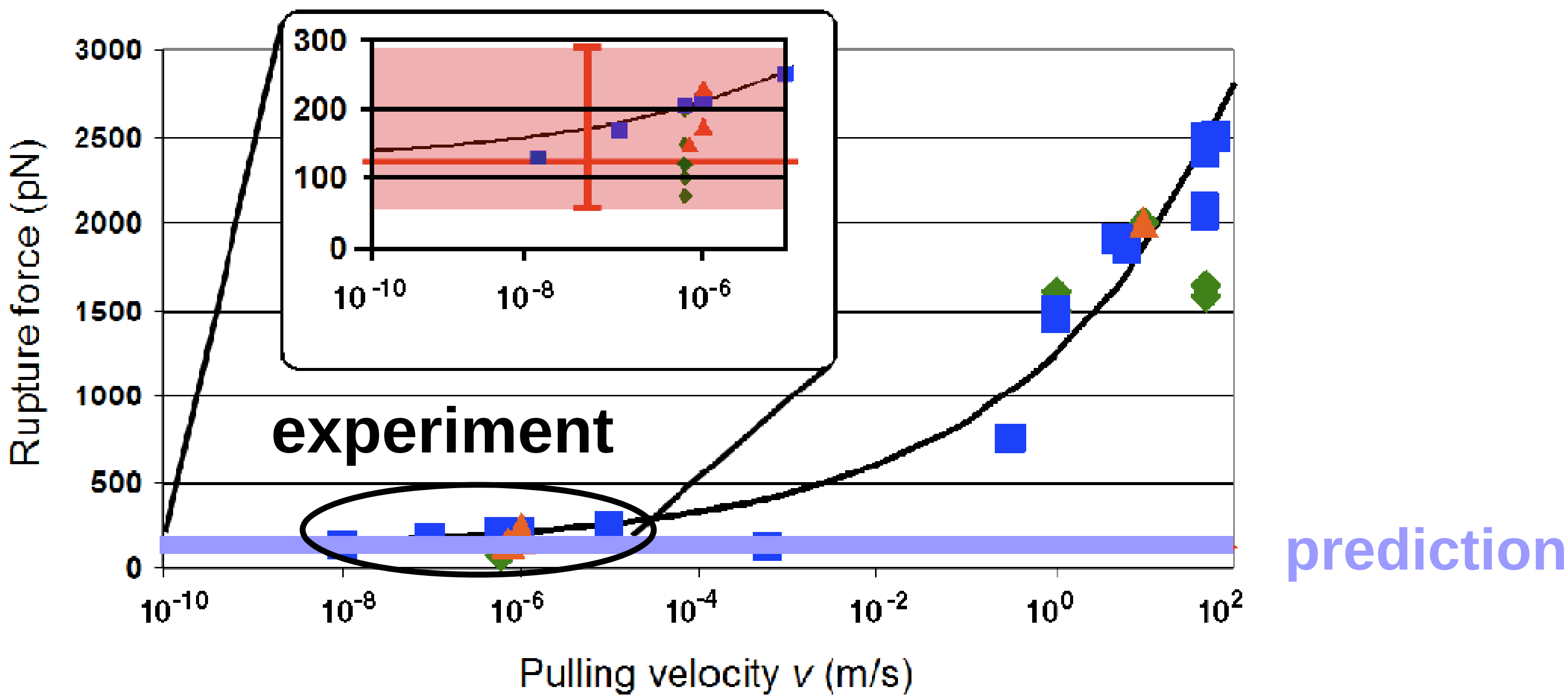




Keten and Buehler, *Physical Review E,* 2008

Validation against experiment

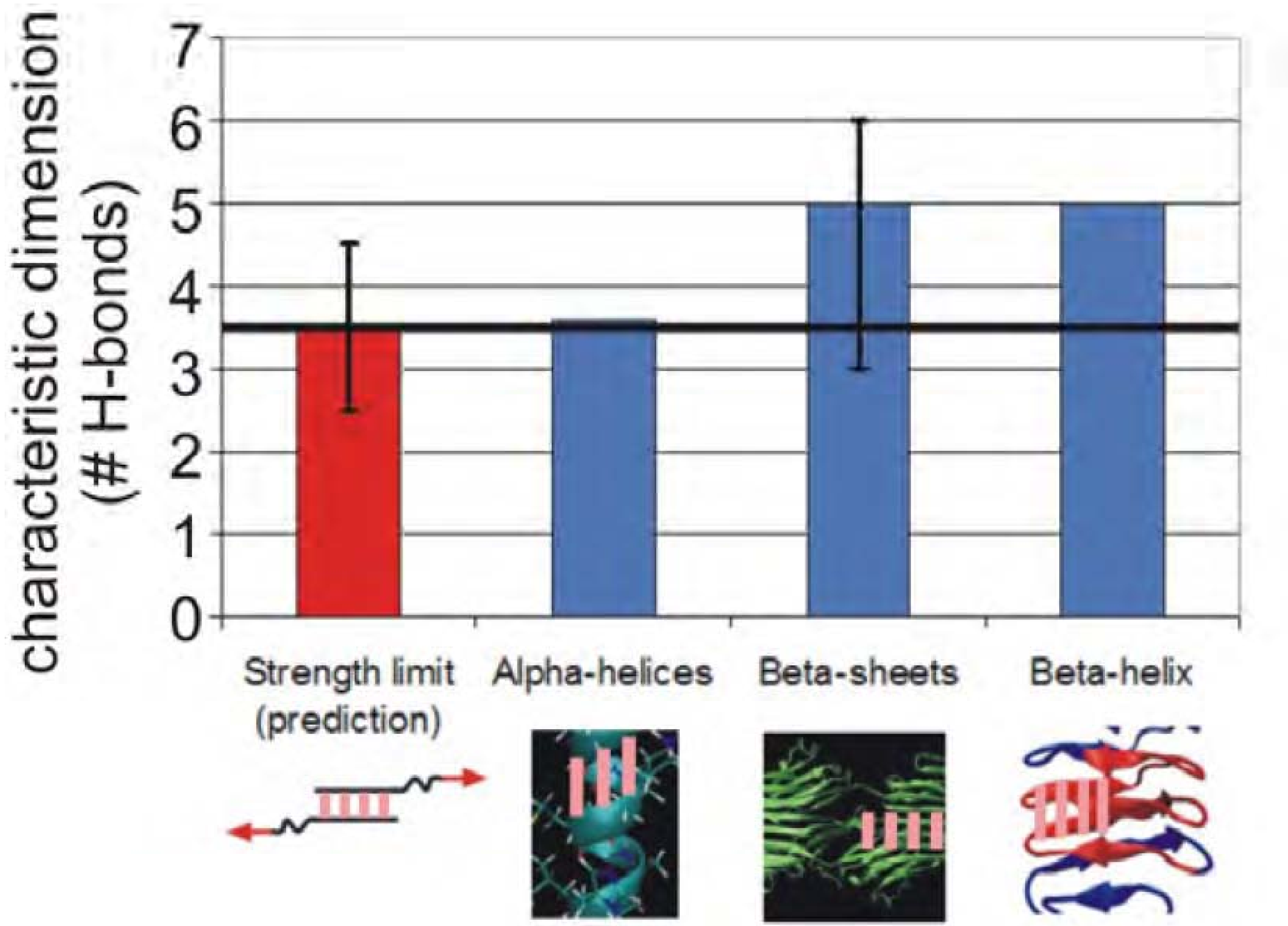
Simple model explains **many** experiments,
has implications for a wide range of polymeric materials



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

Keten and Buehler, *PRL*, 2008, Ackbarow, Keten *et al., J. of Phys. Cond. Matt*., 2009

Cluster size in natural protein materials



S. Keten and M.J. Buehler, *Nano Letters, PRL,* 2008*;* M. Buehler and S. Keten, *Rev. Mod. Phys.* 2010

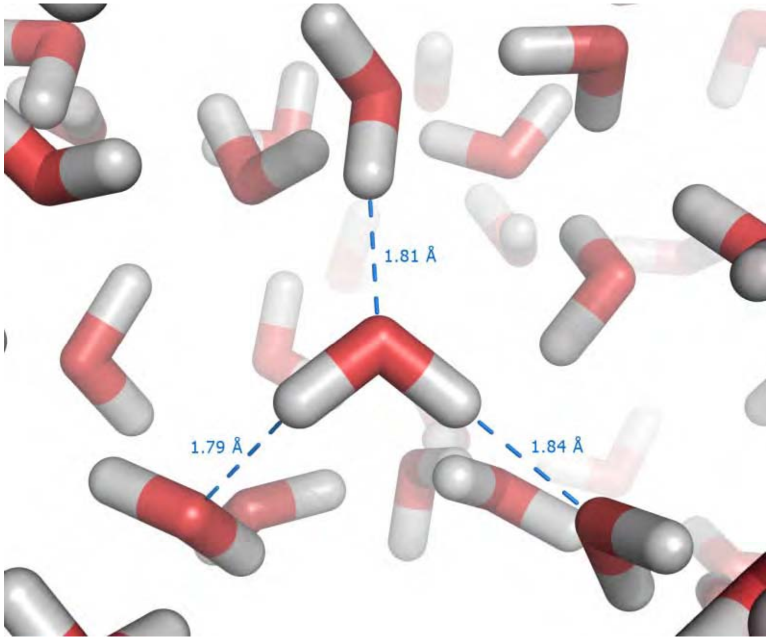
Properties of H-bonds

controls unique properties of water

Water: liquid @ 300K

Protein: solid @ 300K

WHY?



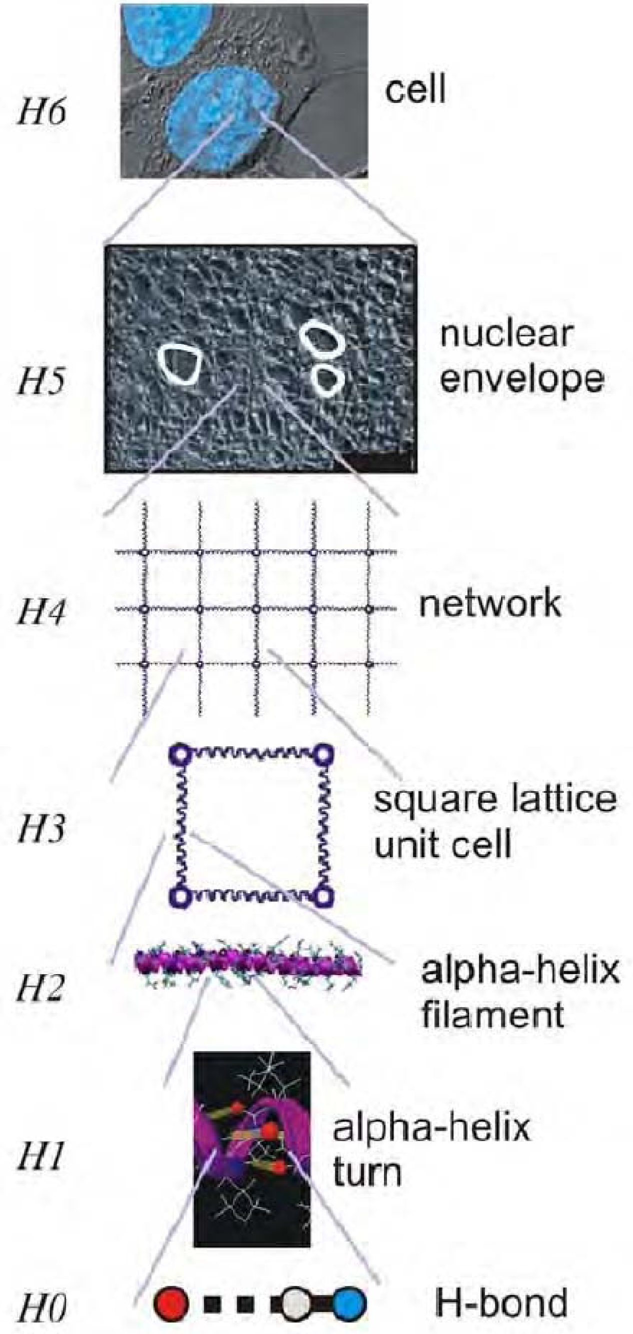
H-Bond energy: 2-10 kcal/mol

Thermal energy scale

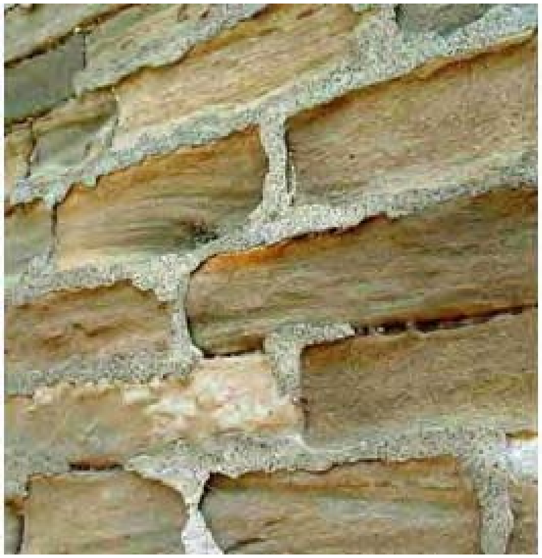
$k_B T \approx$ 0.6 kcal/mol (room temp)

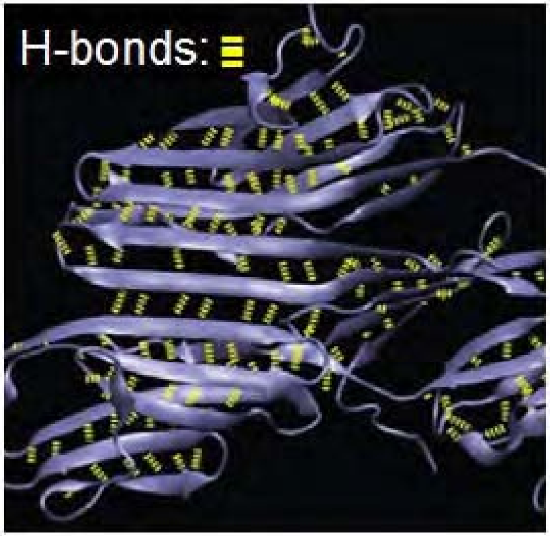
individual H-bonds in water

Hierarchical assembly – from nano to macro

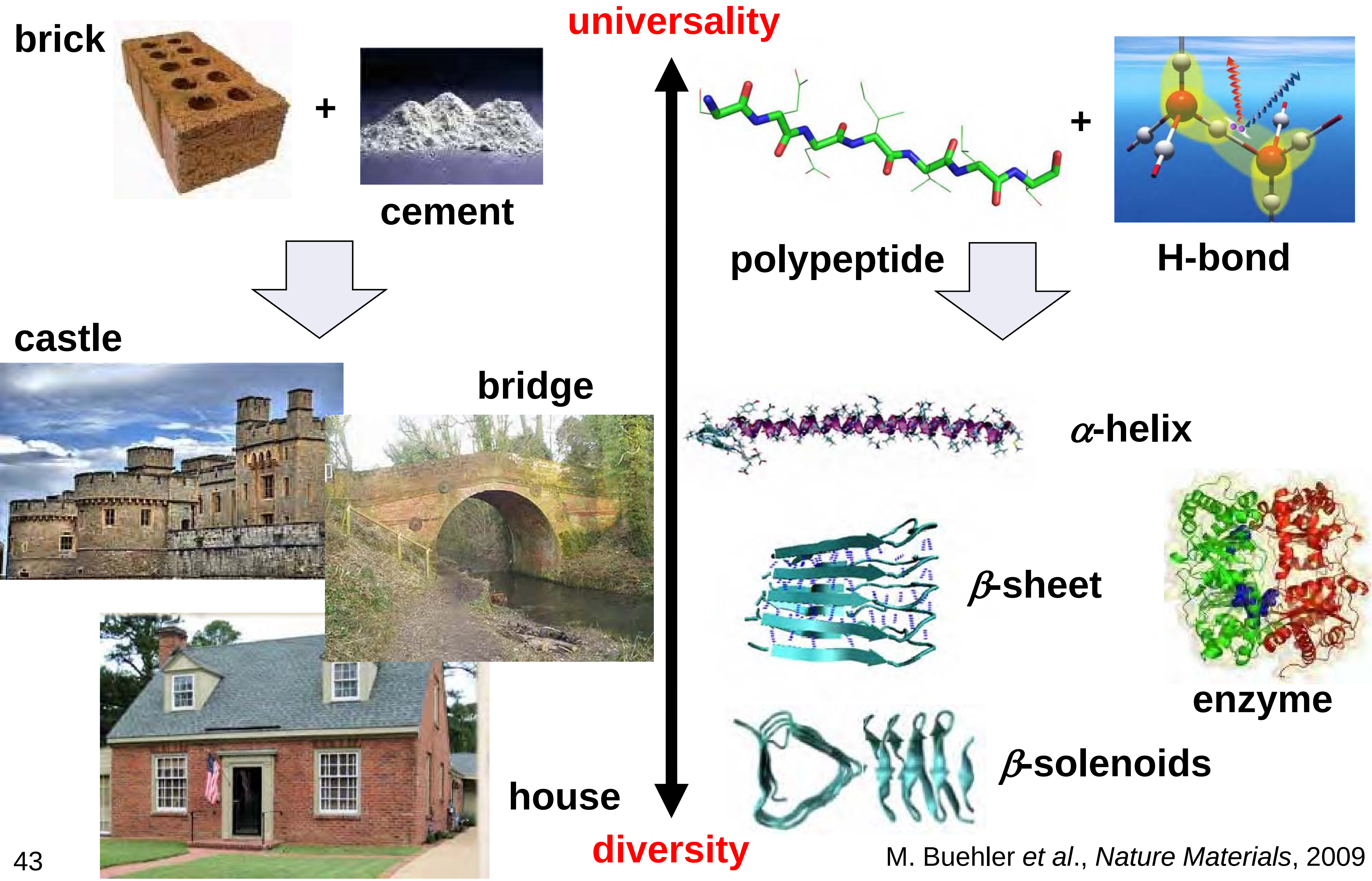


- Protein filaments and protein materials constitute hierarchical assemblies, from nano to macro
- H-bonds provide a "universal glue" found proteins (e.g. alpha-helices, beta-sheets, etc.) – **Nature's cement**
- Fundamental question—mechanical properties of H-bonds



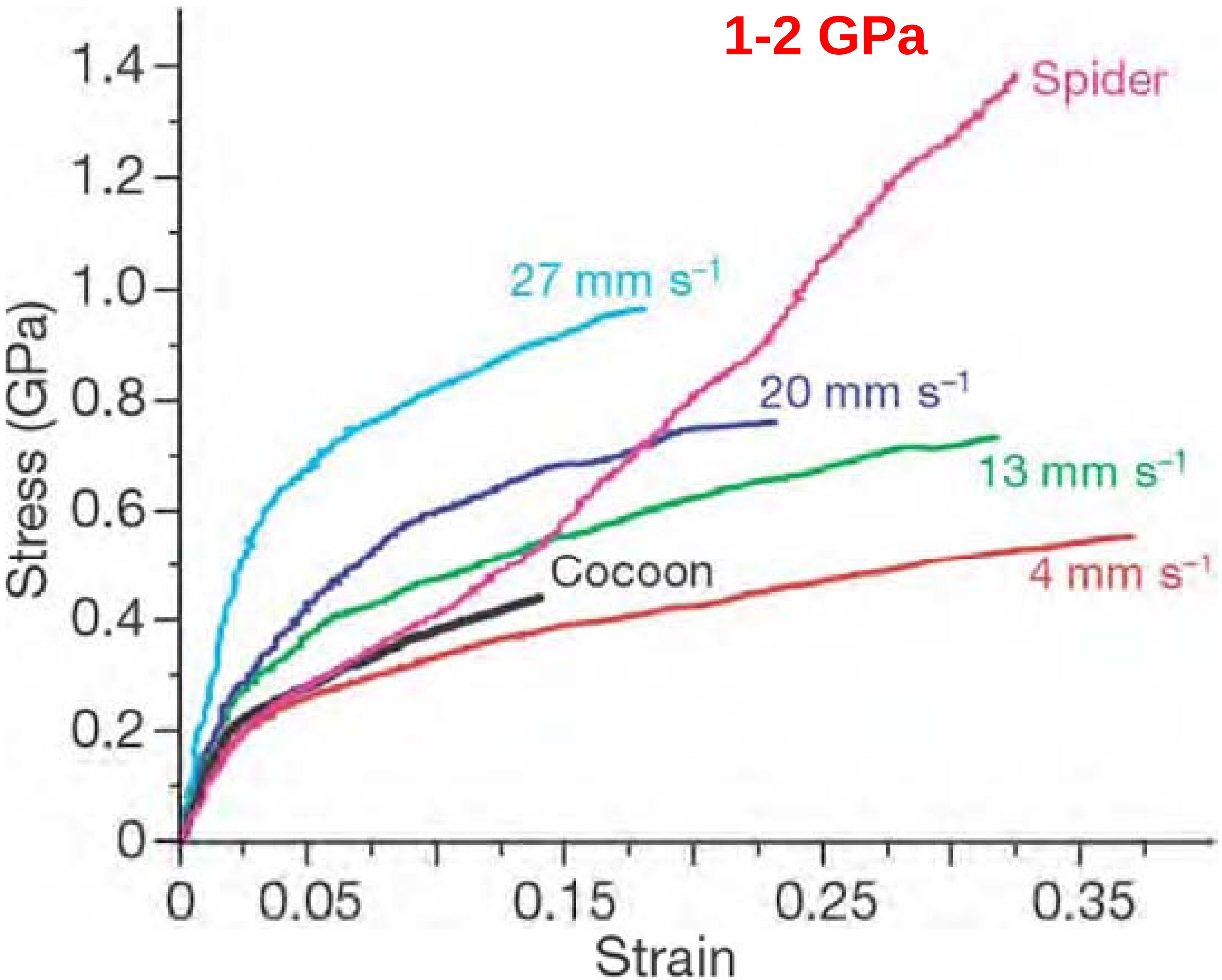


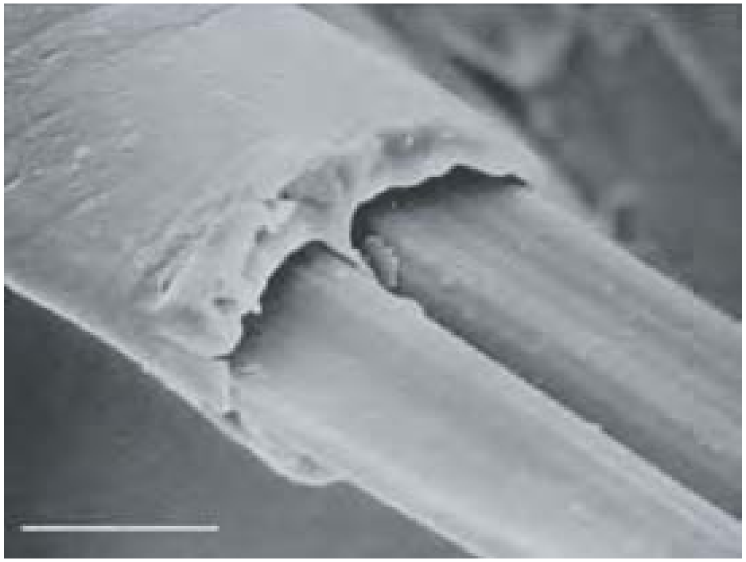
Universal building blocks, diverse structures (and thus, functions)



M. Buehler *et al.*, *Nature Materials*, 2009

Mechanical response of spider silk

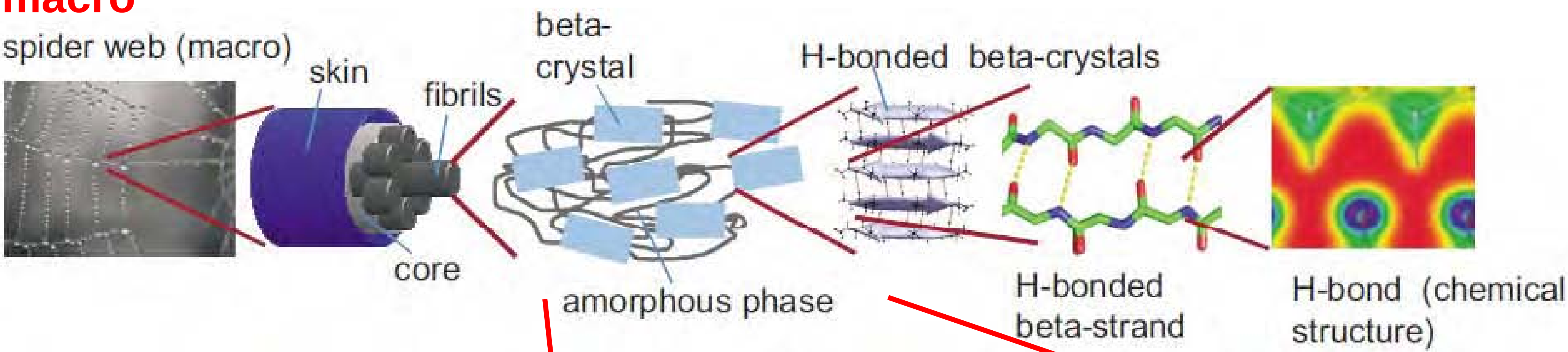




Z. Shao and F. Vollrath, *Nature*, 2002

Spider silk's hierarchical structure

macro

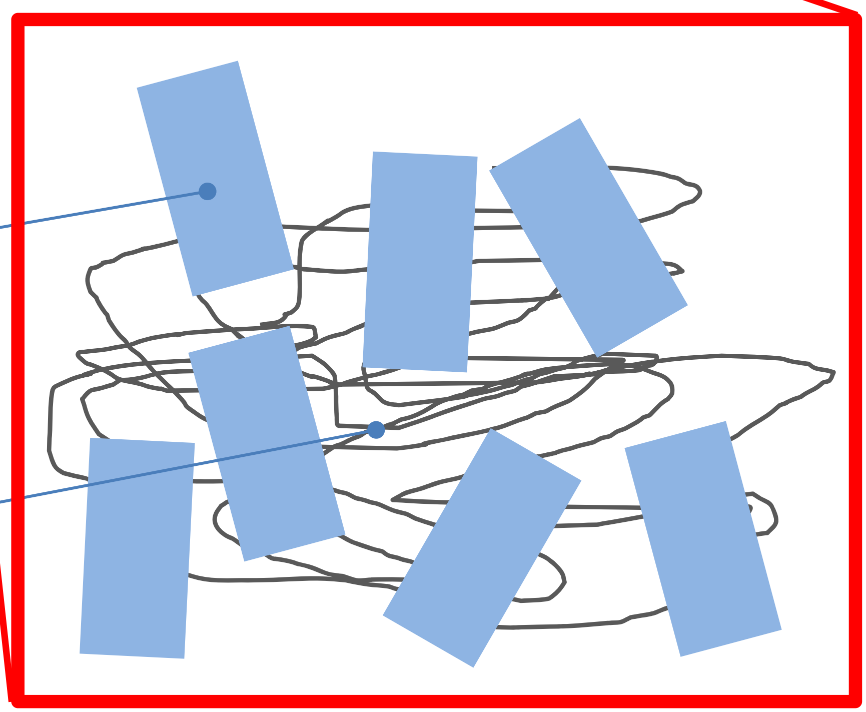


nano

Molecular structure ???

beta-crystal

amorphous phase

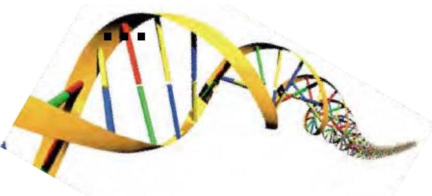


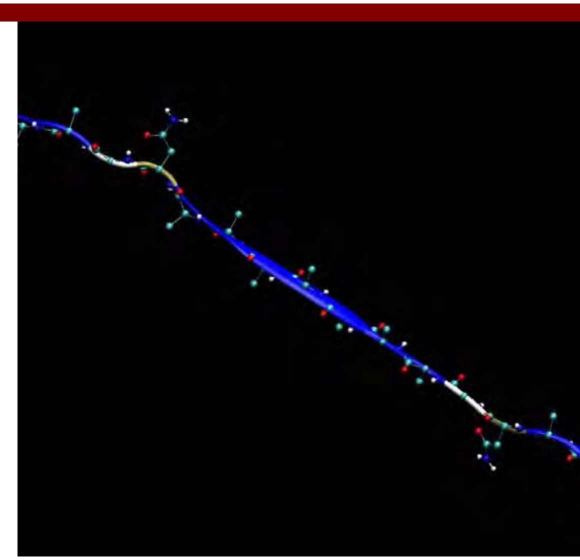
S. Keten, M. Buehler,
APL, 2010

Structure prediction and functional properties

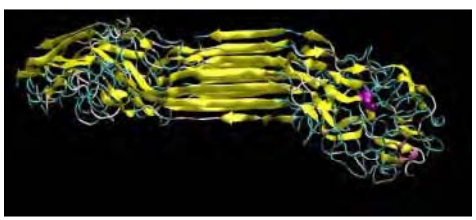
Genetics

…GGLGGQGAGA AAAAAGGAGQG

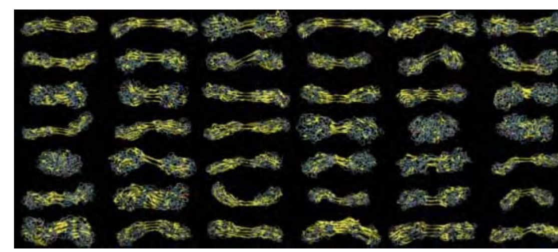


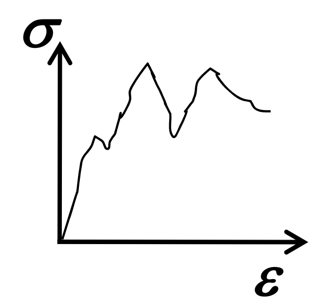


Amino acid sequence → **Replica Exchange Simulations** → **Ensemble of final structures** → **Validation (experimental results)** → **Mechanical characterization (multiscale)**



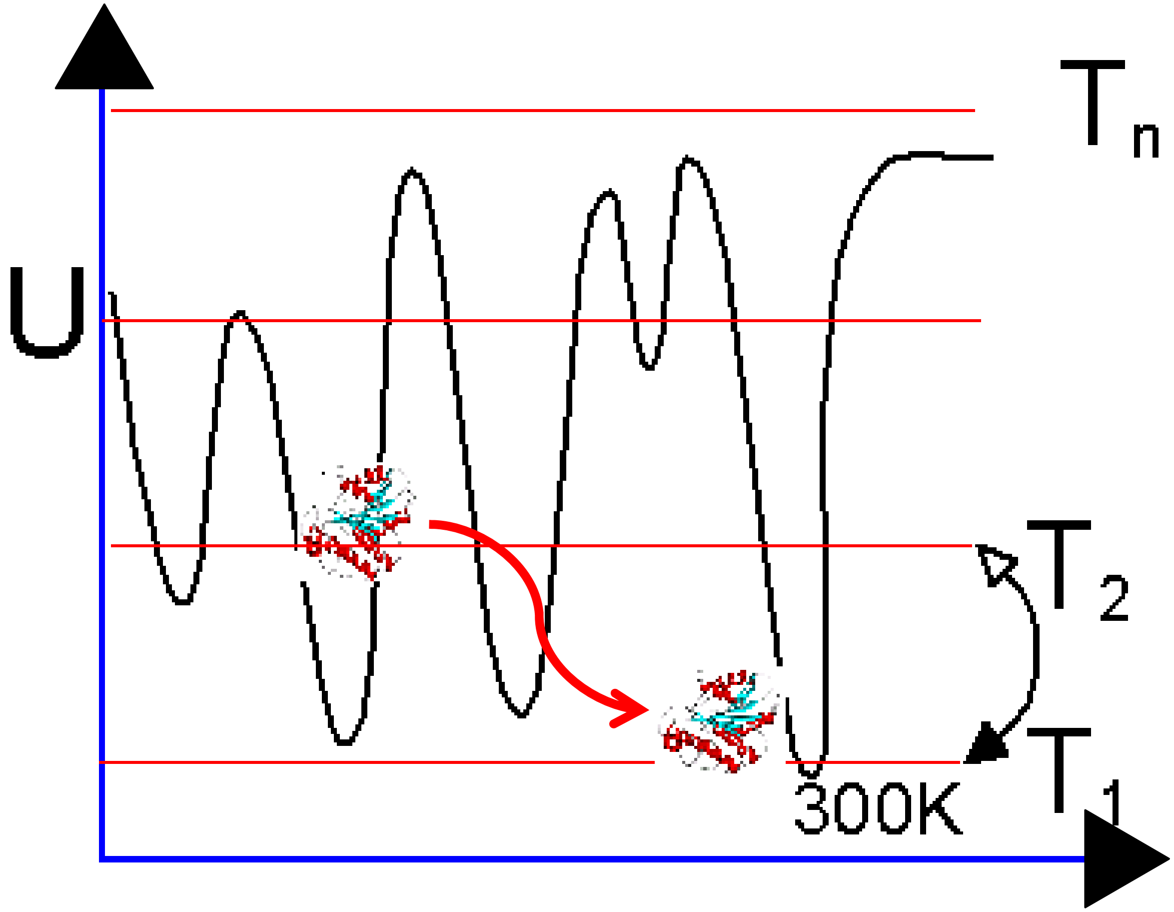
Structure

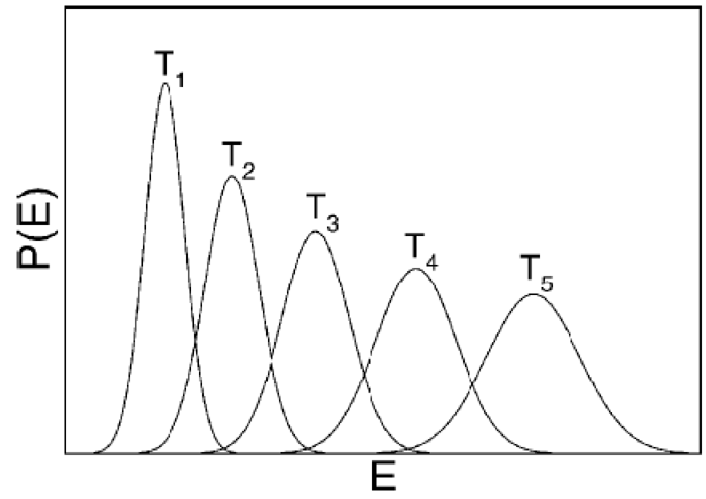




Mechanics (functionality)

Replica Exchange approach (parallelized)



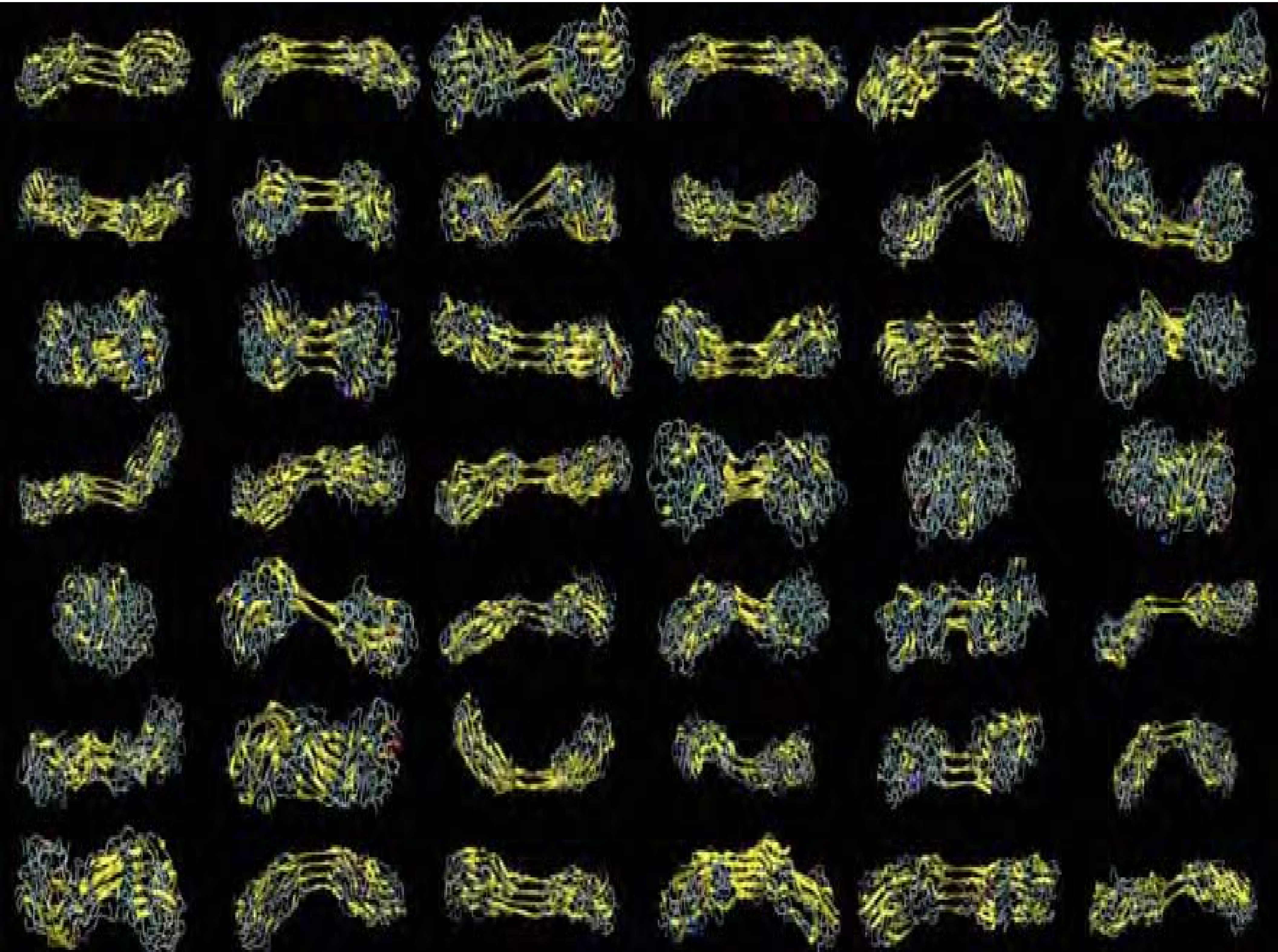


Simulate copies of same system with different temperatures

Exchange configurations between them

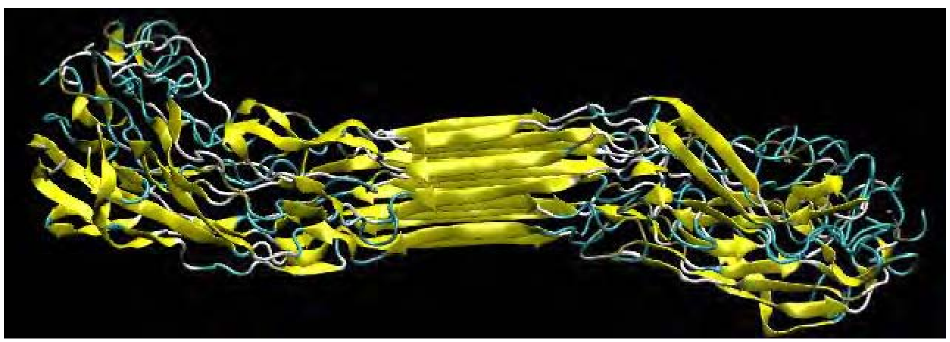
Evaluate most stable configurations obtained at low temperature = **solution "ensemble" of structures**

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

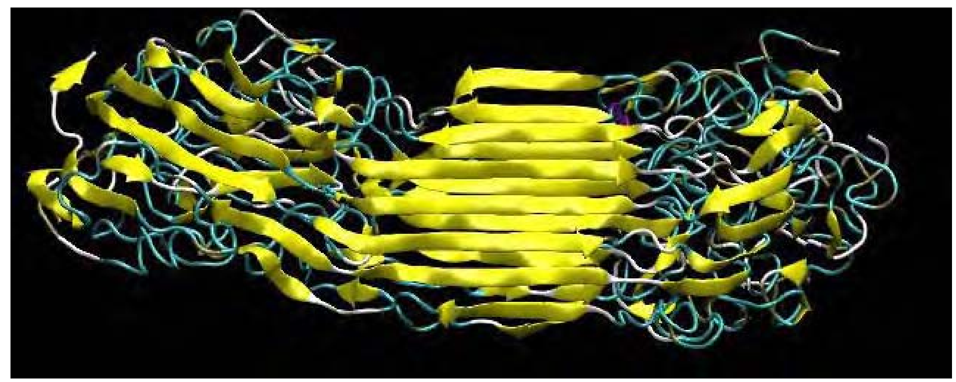


Search for most likely conformations

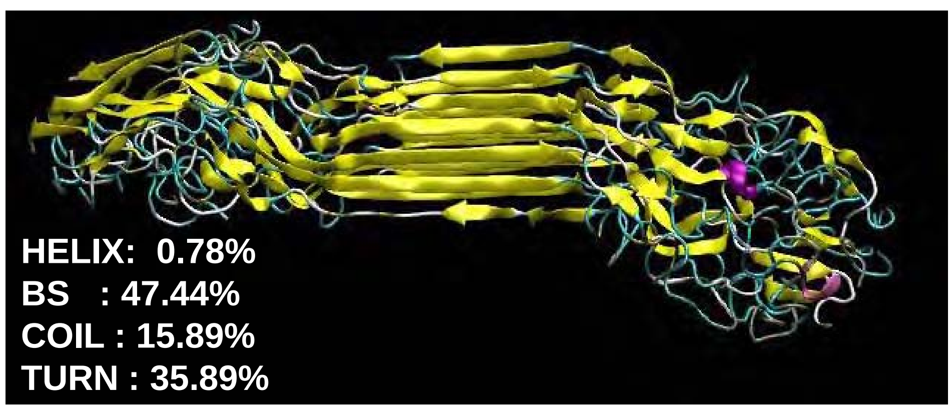
Key finding: Secondary structure is dominated by beta-sheets (mostly seen in poly-Ala regions), as well as turn type structures. This is in line with what has been observed in spider silk. (% below show relative amount of respective secondary structure)



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

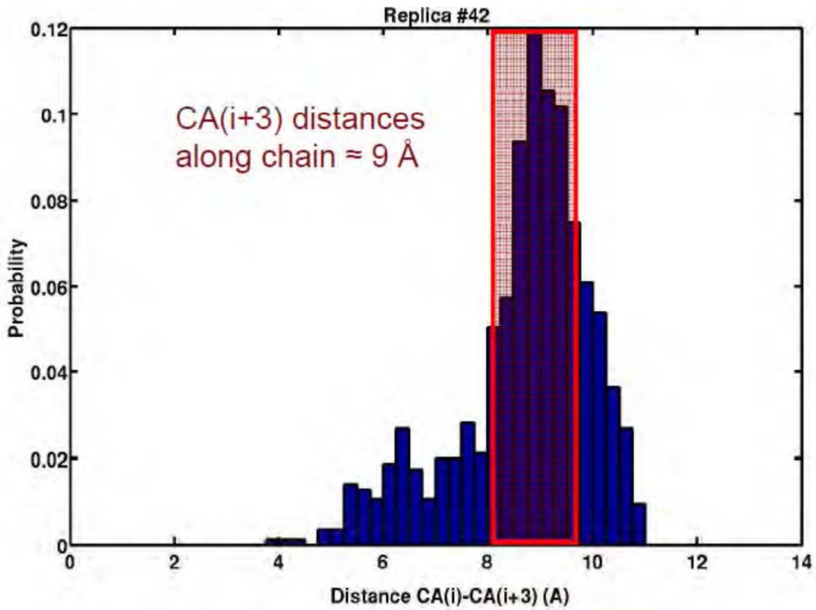


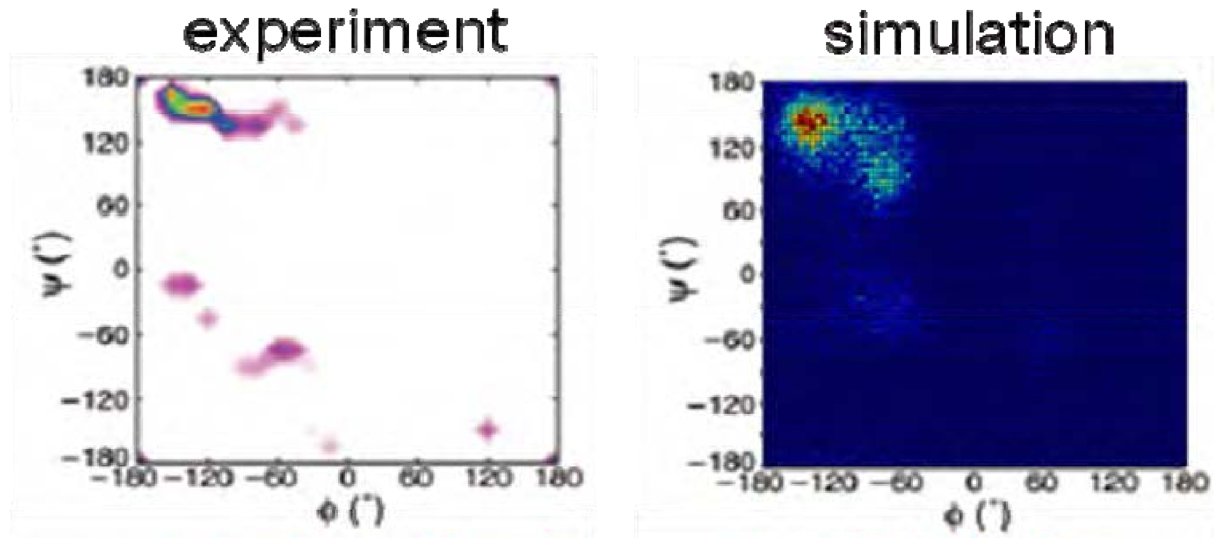
HELIX: 0.44%
BS : 40.44%
COIL : 15.67%
TURN : 43.44%



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

Experimental validation





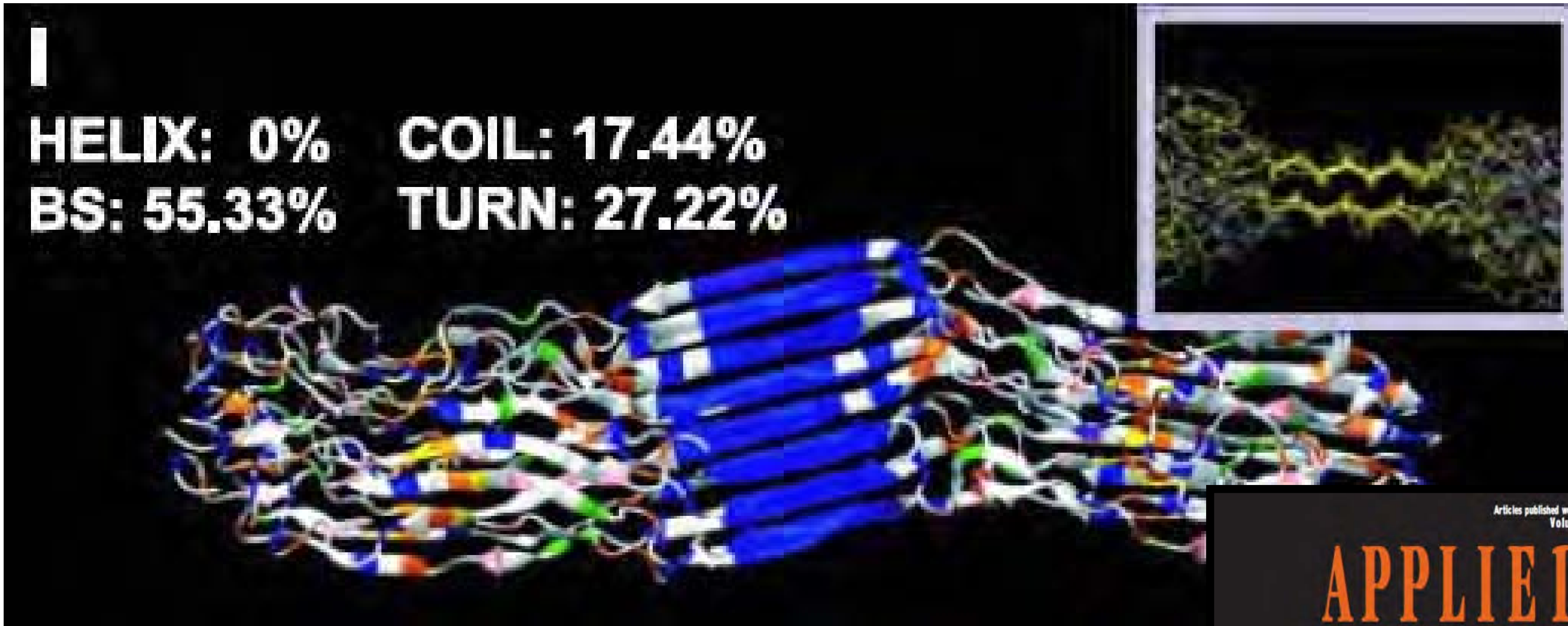
alanine dihedral angle distribution

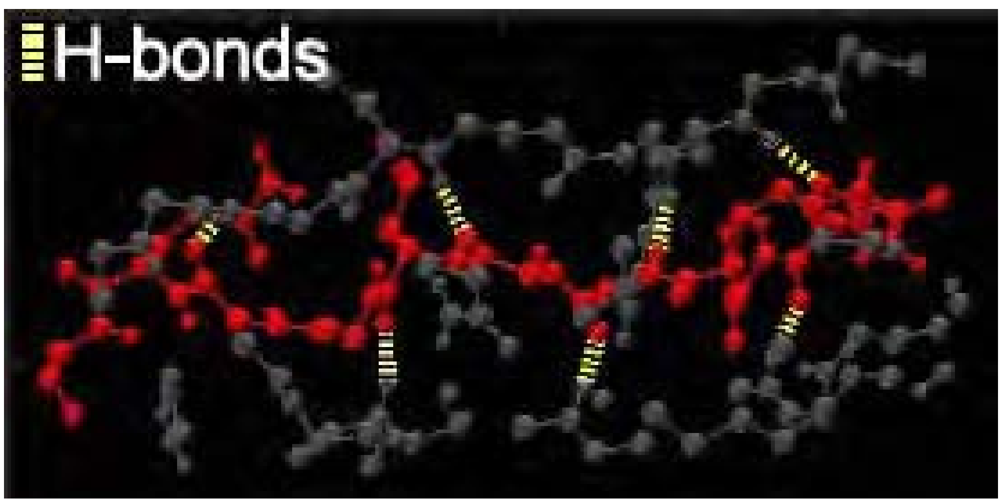
- poly-Ala regions form beta-sheet regions with stacking to accommodate methyl side-chains. These interlocked regions are densely packed and orderly.

- 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.

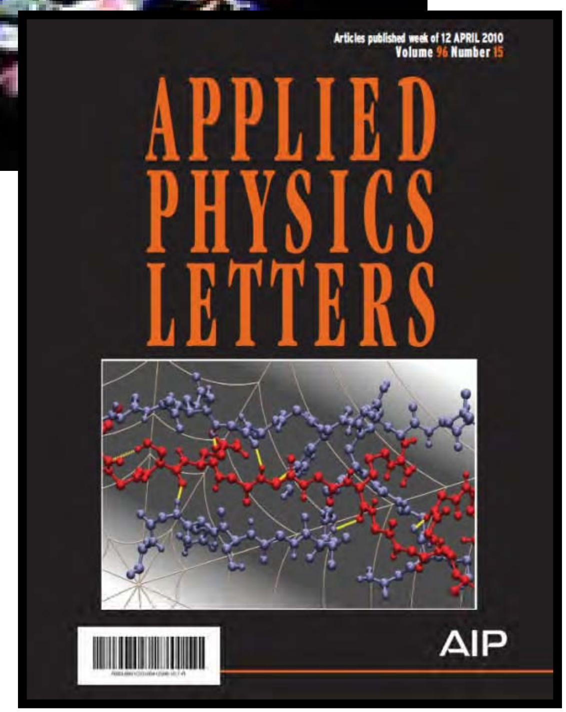
S. Keten, M. Buehler, *APL,* 2010

Detailed view of structure





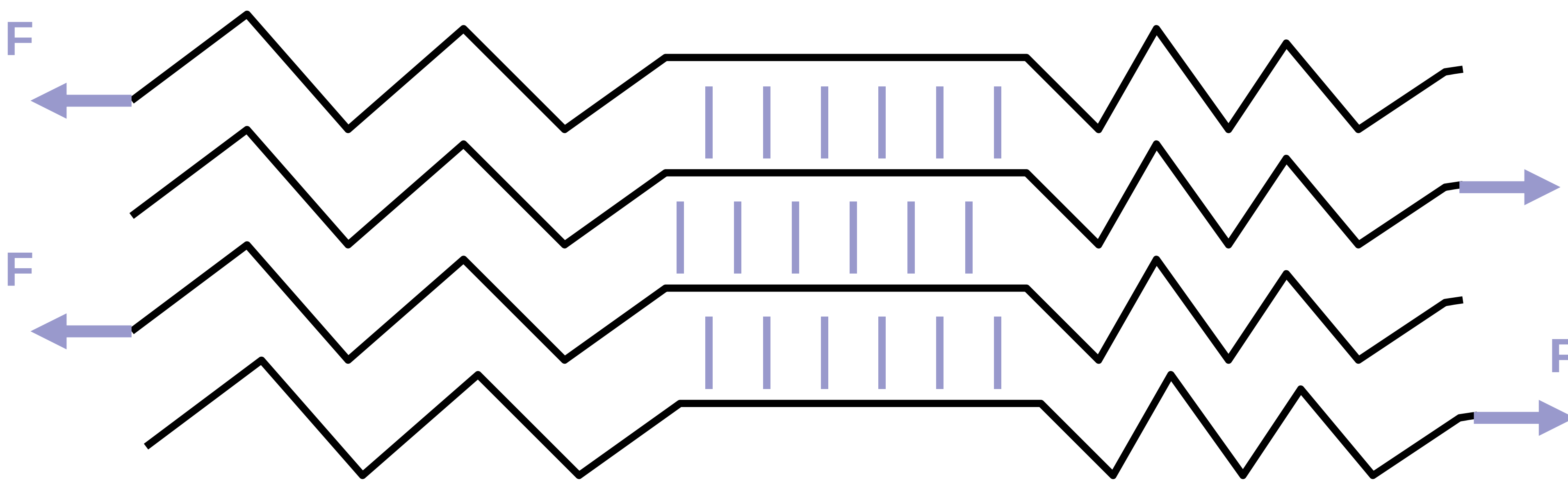
3_1 helix



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

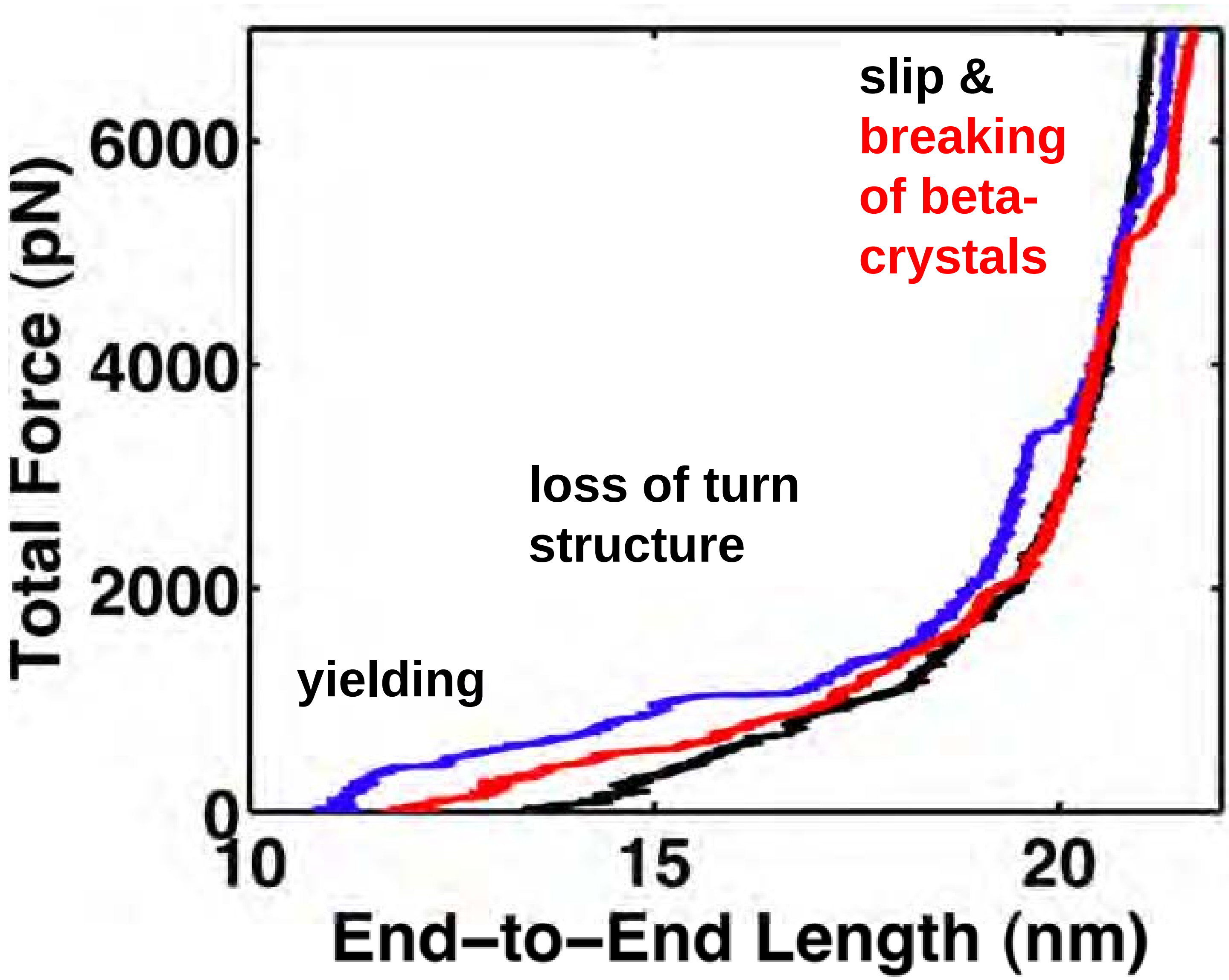
Mechanical analysis of spider silk

- 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 nm^2 for all systems



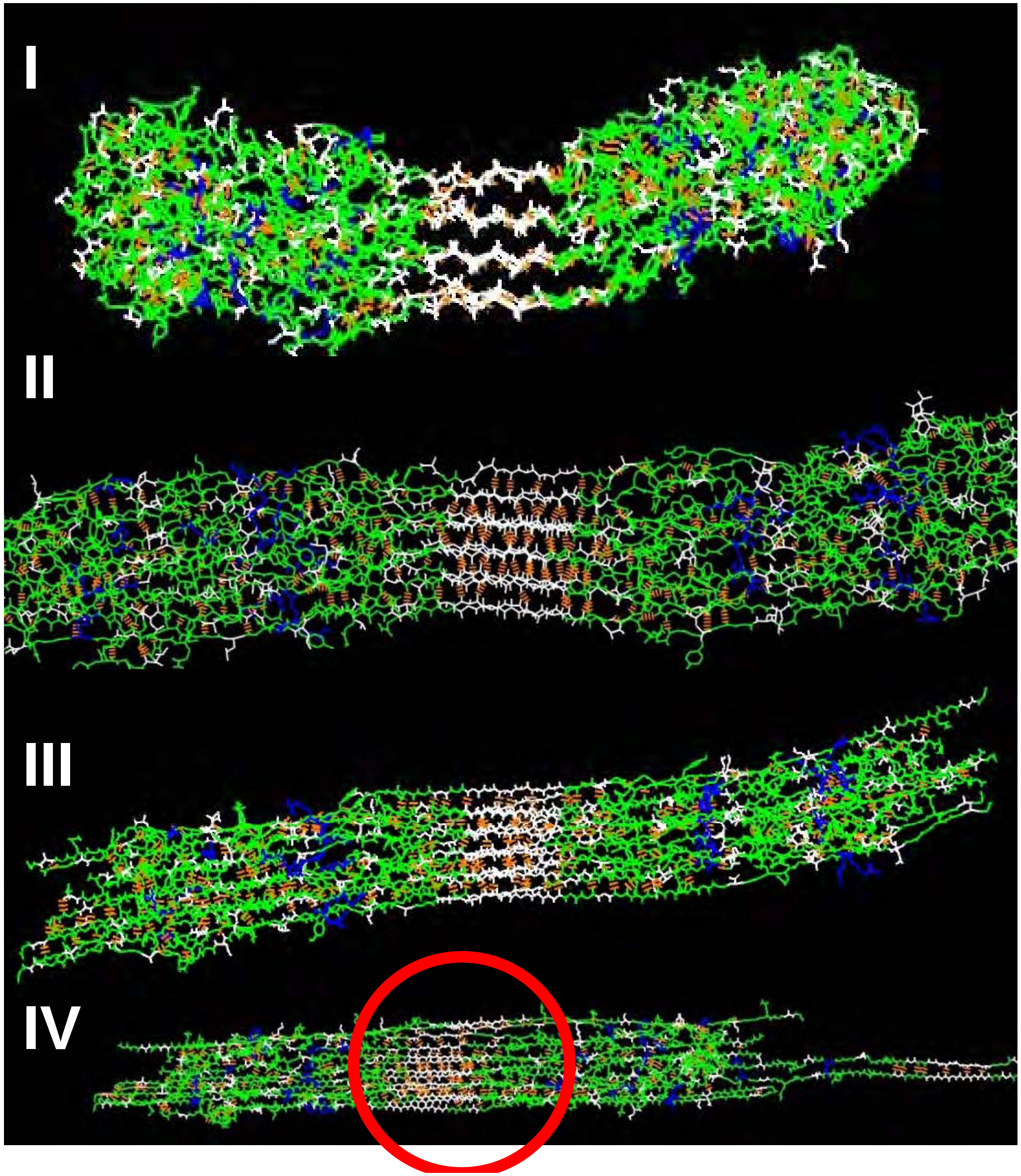
S. Keten, M. Buehler, *APL,* 2010

Force-deformation behavior



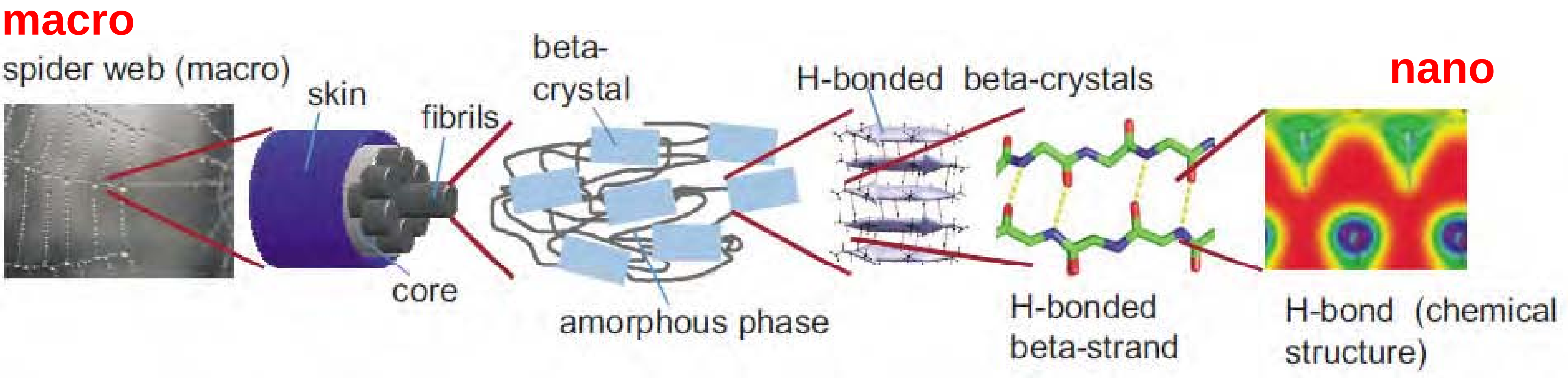
S. Keten, M. Buehler, *J. Roy. Soc. Interface,* 2010

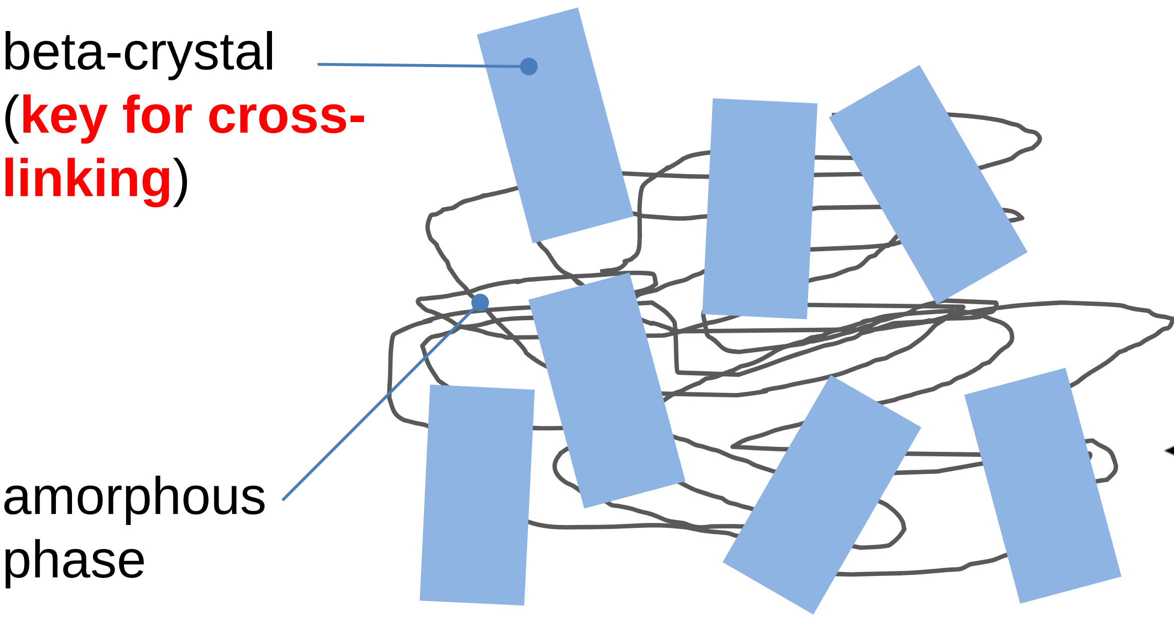
Deformation analysis of spider silk

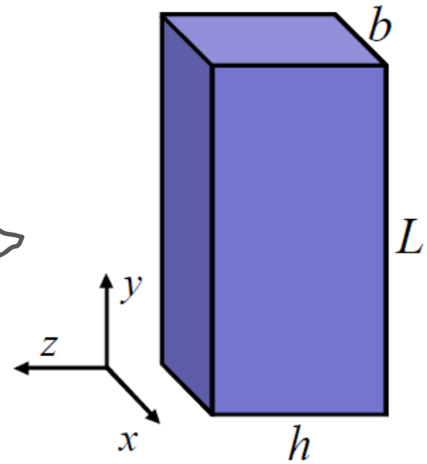


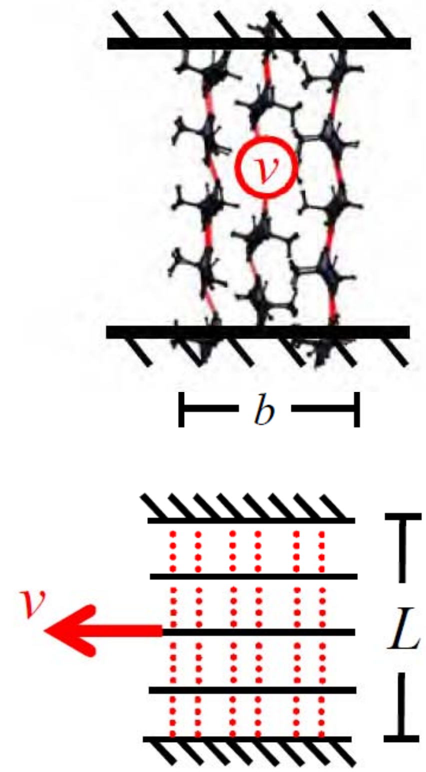
S. Keten, M. Buehler,
J. Roy. Soc. Interface,
2010

Spider silk's hierarchical structure



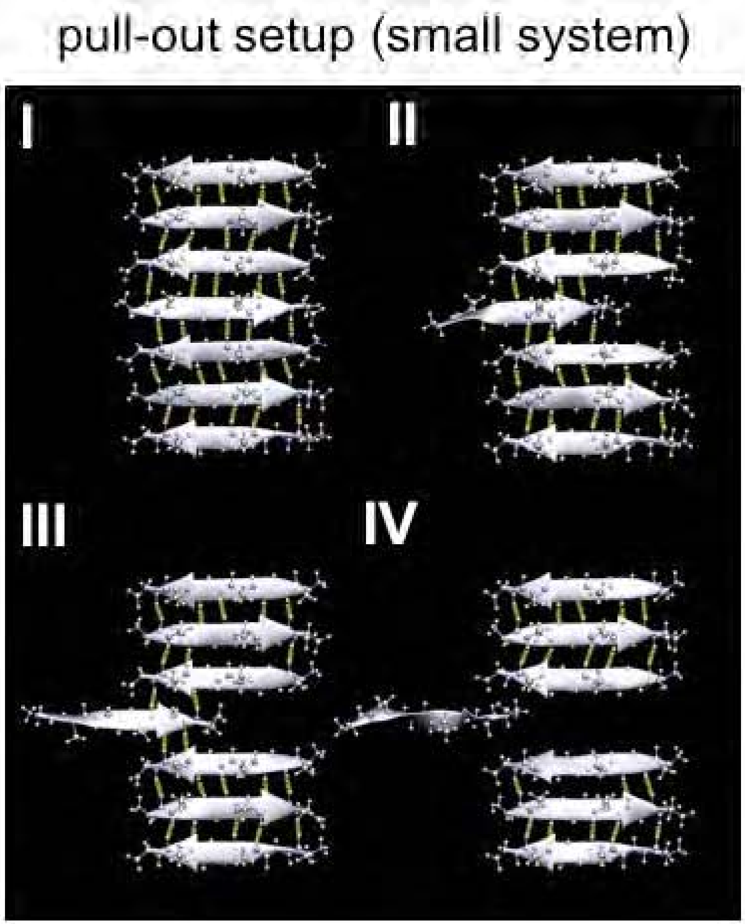




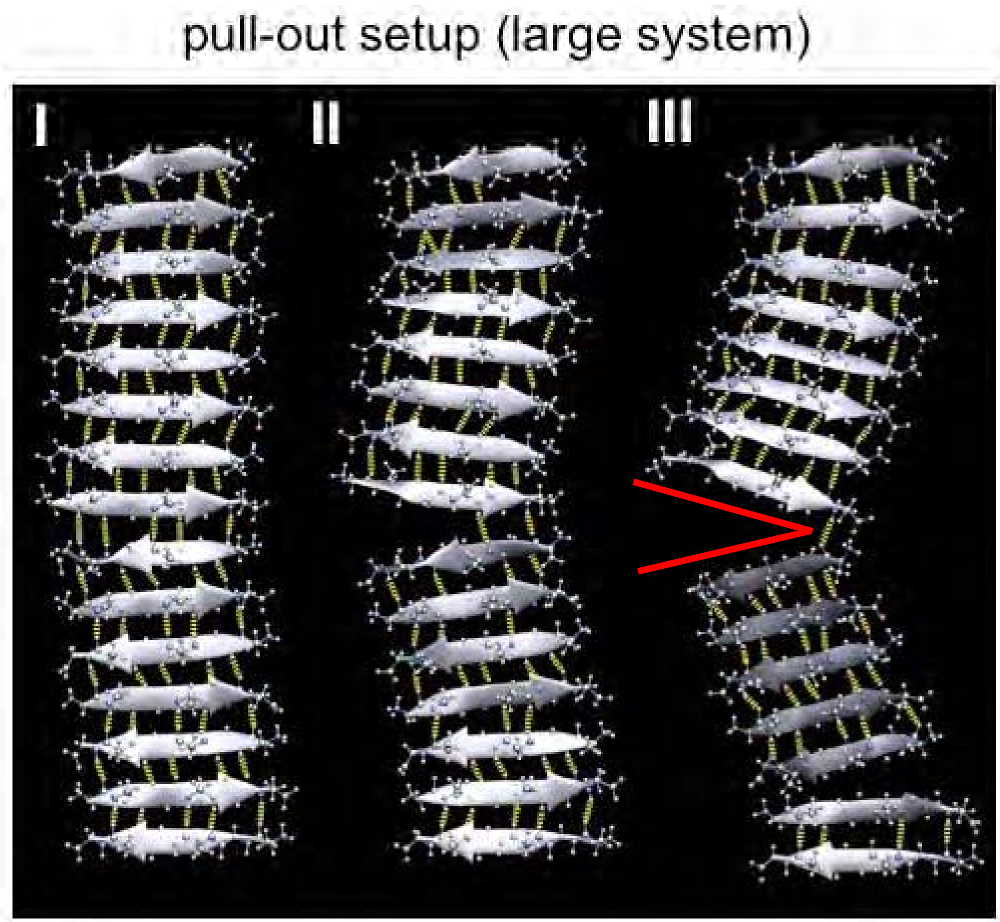


Keten, Xu, Ihle, Buehler, *Nature Materials,* 2010

Size effects in silk nanocrystals



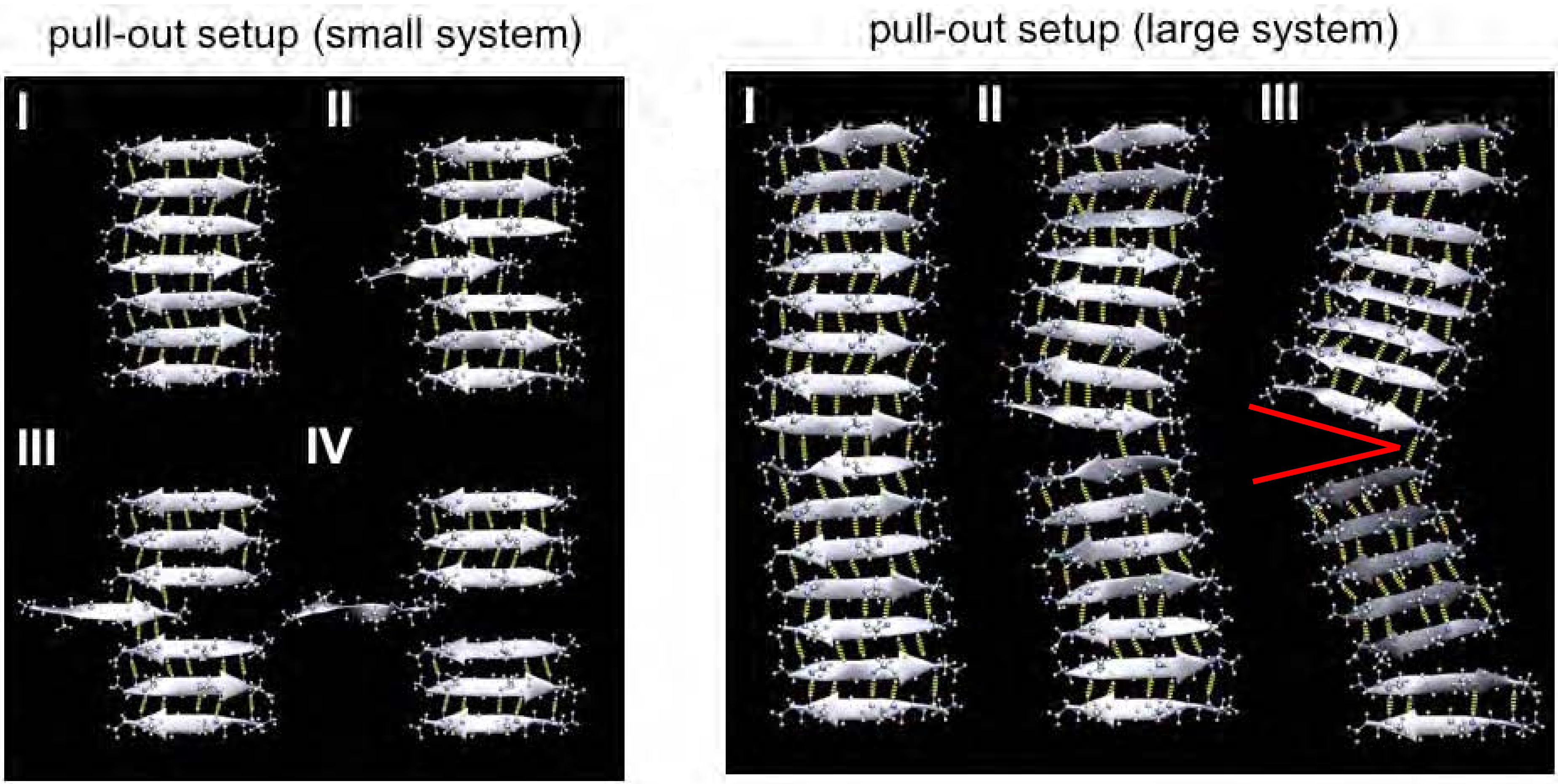
stick-slip mechanism

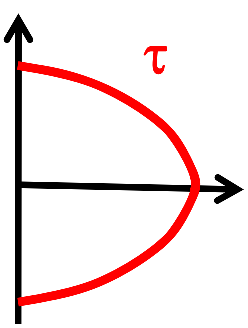


crack formation & propagation

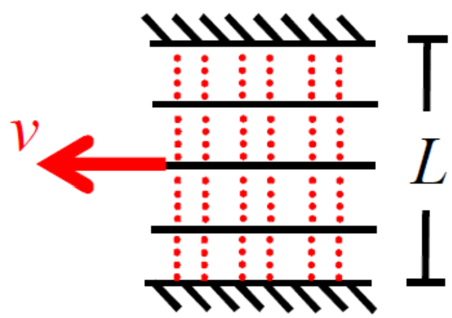
Keten, Xu, Ihle, Buehler, *Nature Materials,* 2010

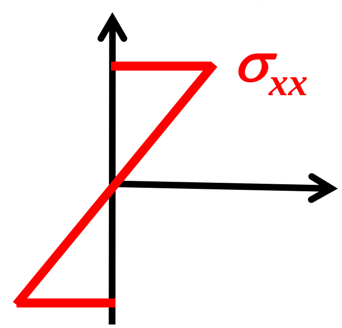
Size effects in silk nanocrystals





shear dominated



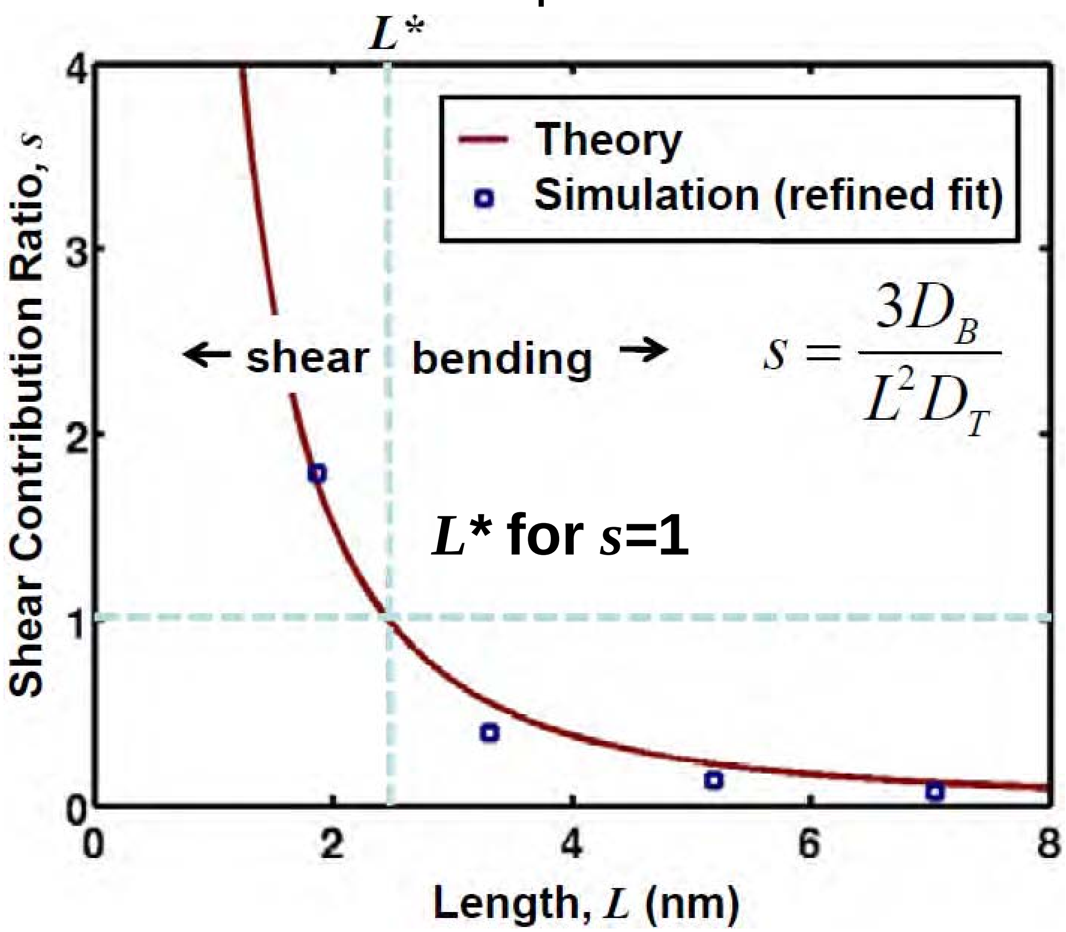


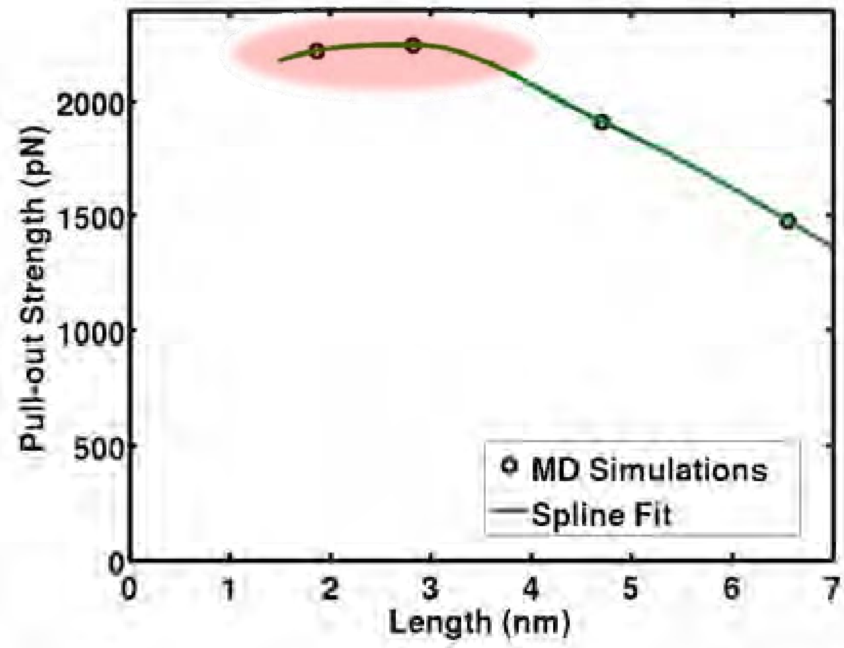
tension/ compression dominated

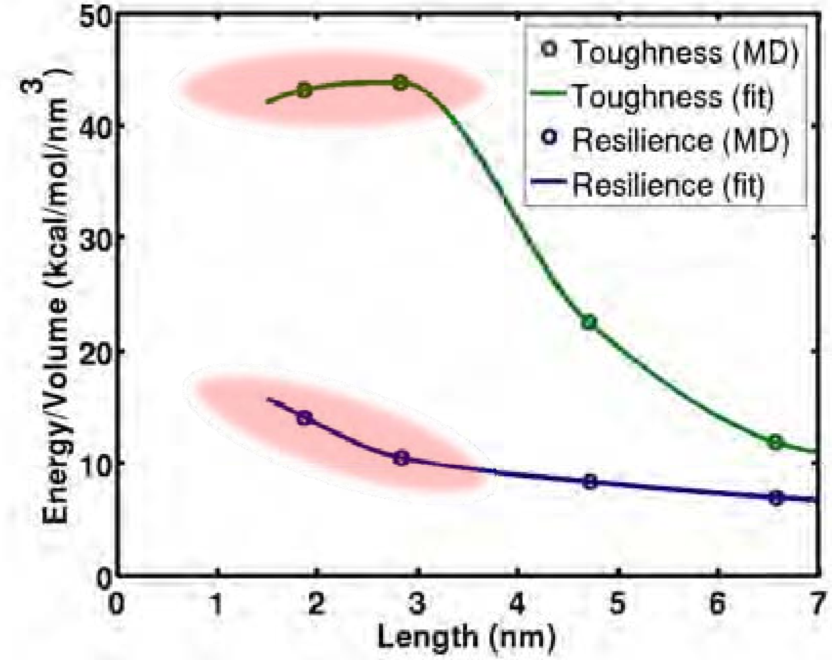
Keten, Xu, Ihle, Buehler, *Nature Materials,* 2010

Size effects in silk nanocrystals

s = ratio of shear vs. bending contributions to displacement



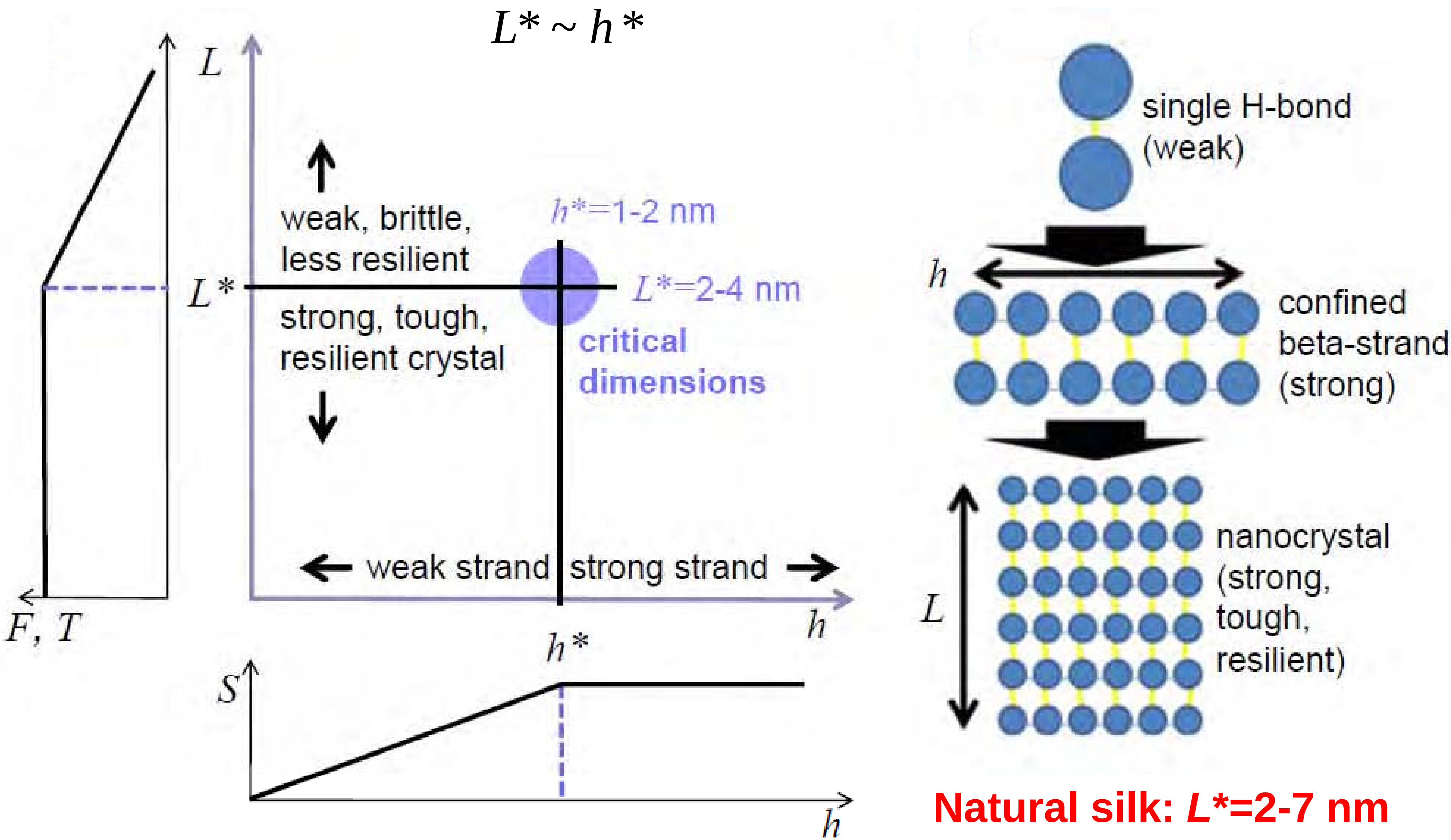




$$s(L) = \frac{3D_B}{L^2 D_T} = \frac{1}{4}\frac{Eh^2}{GL^2} \sim \frac{h^2}{L^2}$$

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

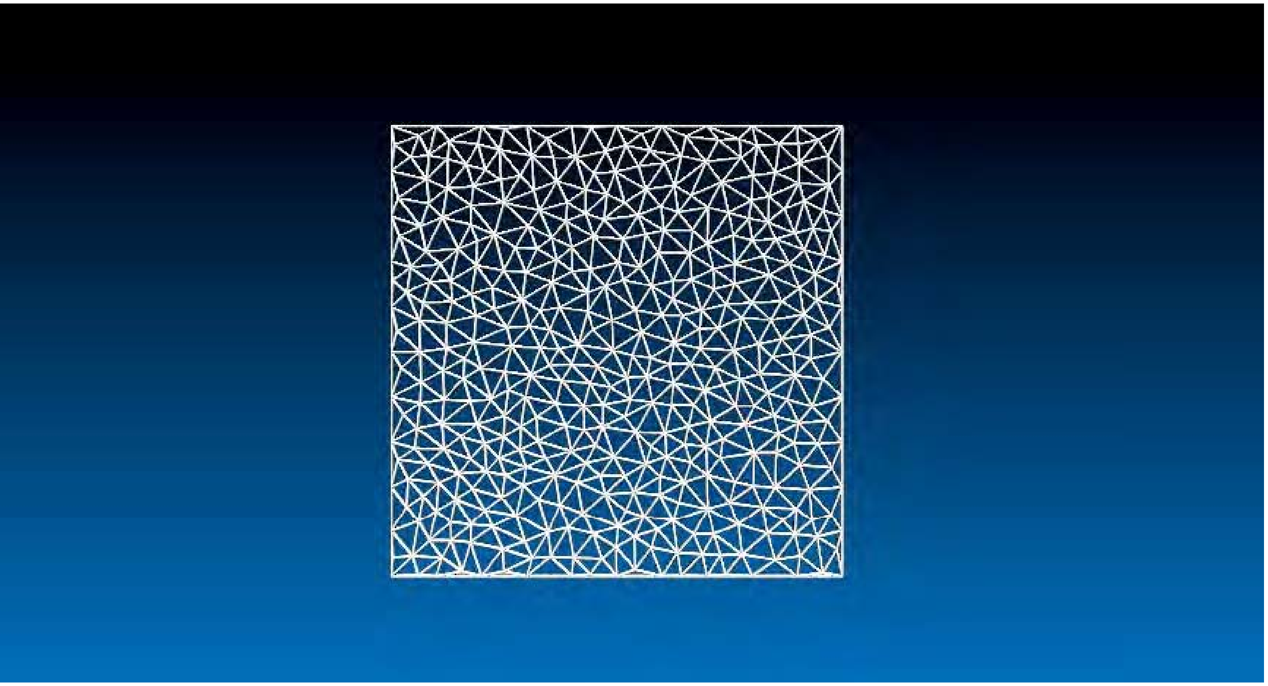
Interplay of scaling laws in spider silk

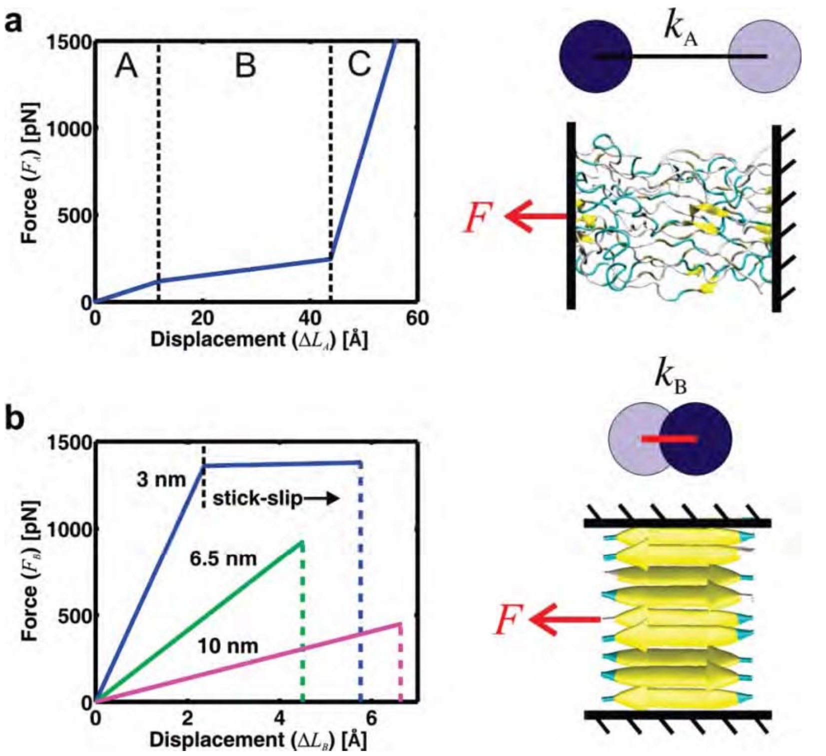


Natural silk: *L=2-7 nm and *h** =2-3 nm**

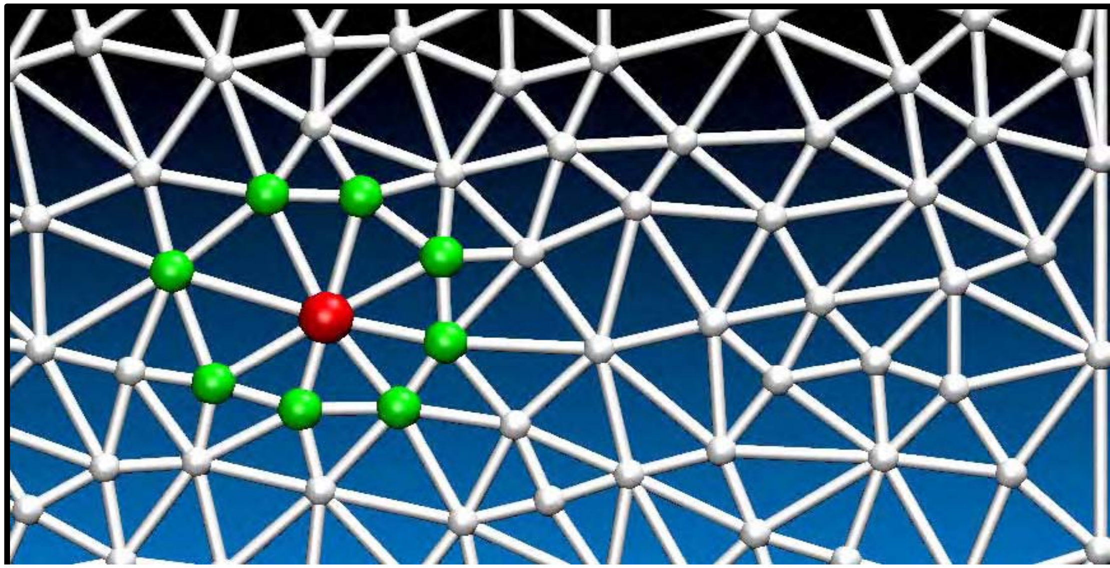
Keten, Xu, Ihle, Buehler, *Nature Materials,* 2010

Larger-scale model of silk (1000 nm)





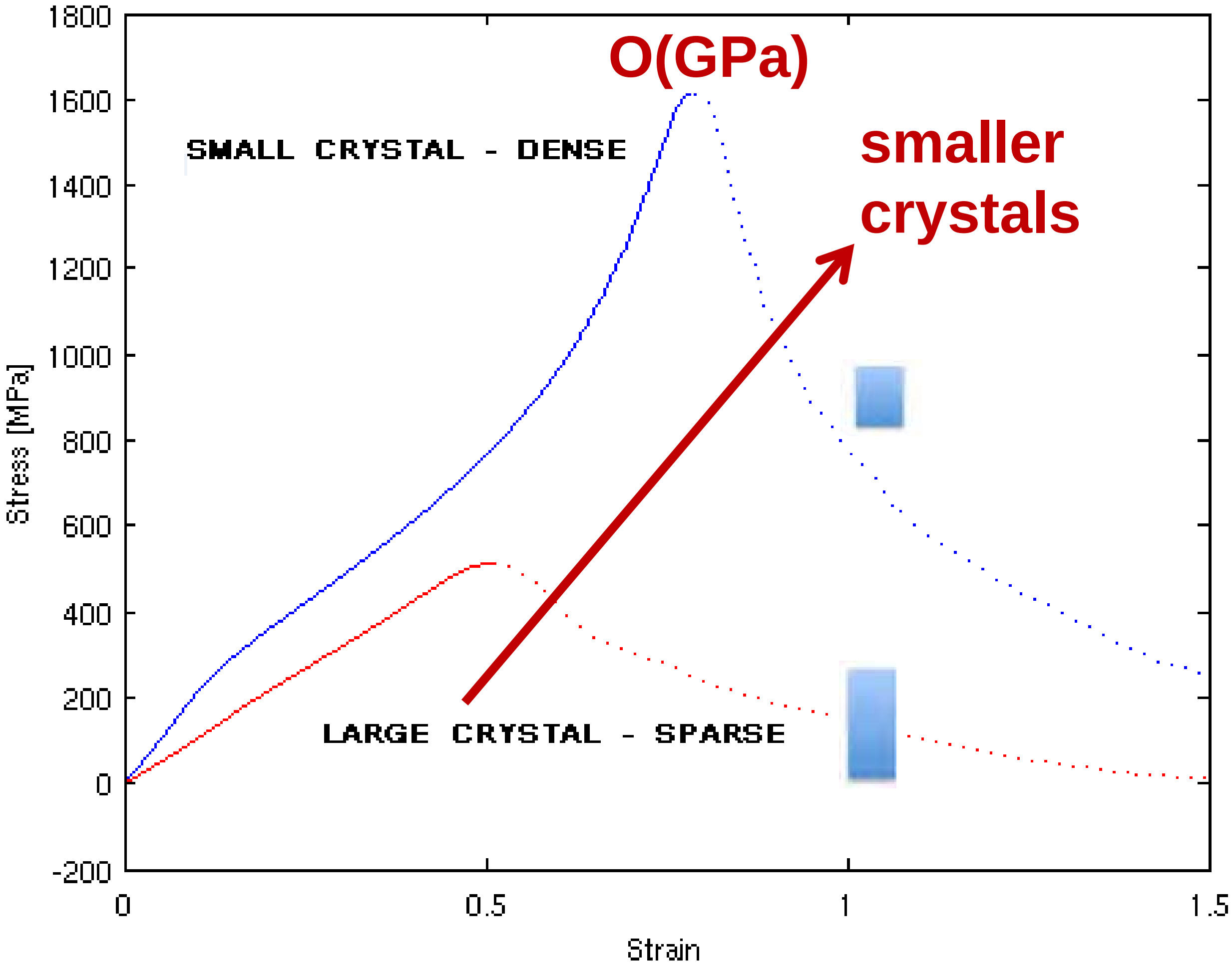
How do nanoscale structures & properties define larger-scale mechanical properties?



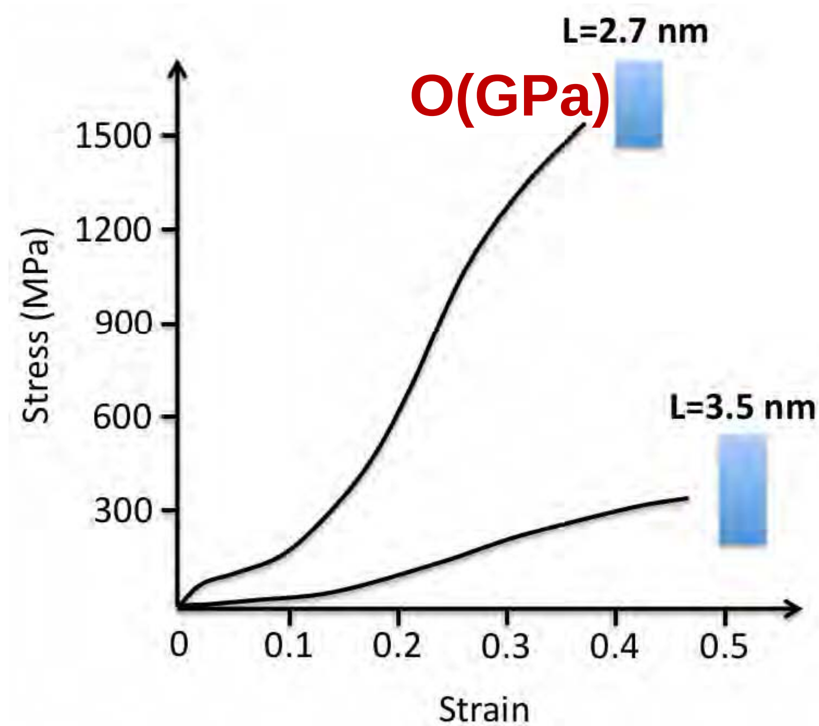
Keten, Nova, Buehler *et al., Nano Letters*, 2010
Nova et al., in preparation

Micro/mesoscale mechanics of spider silk

Simulation



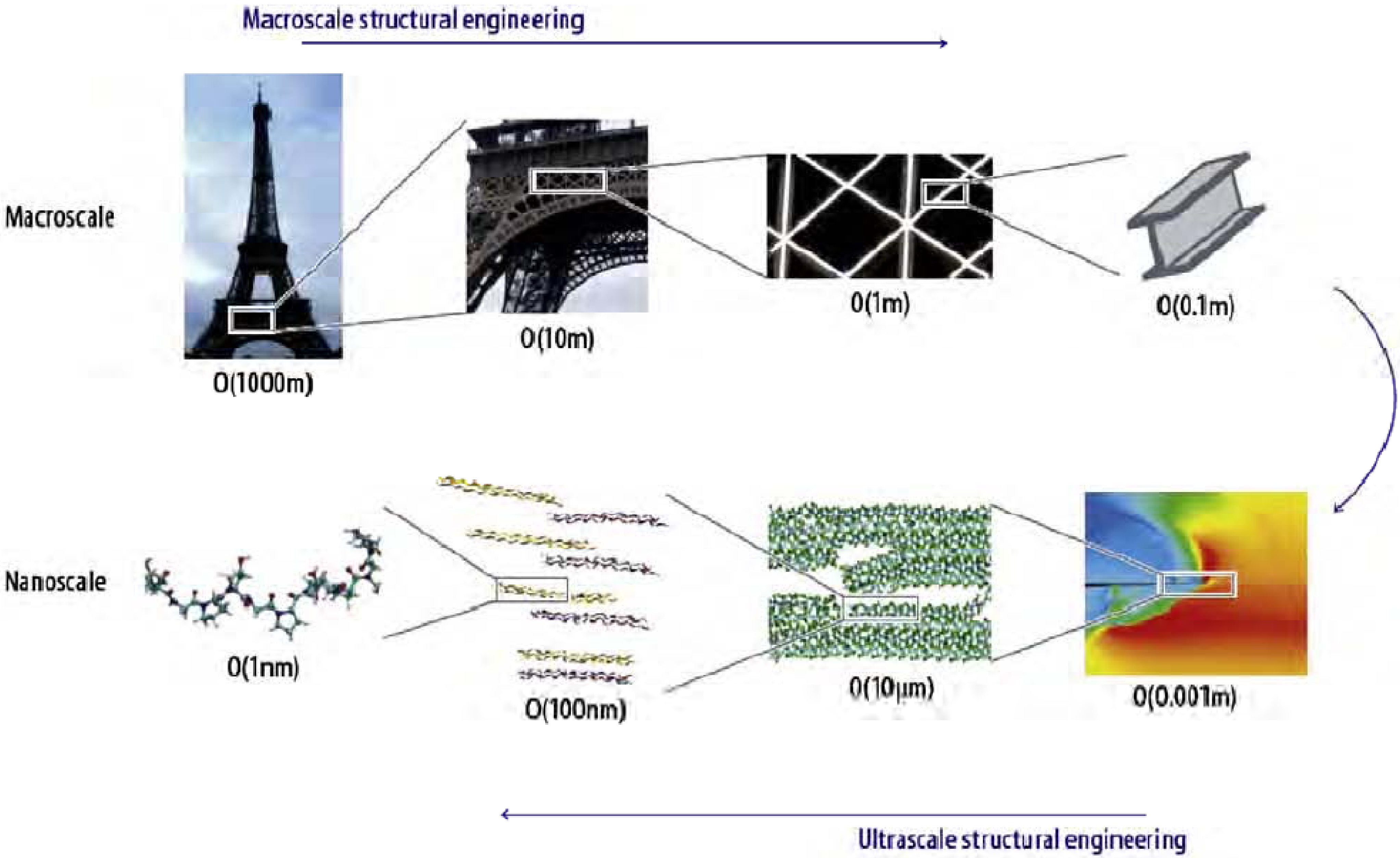
Experiment (N. Du *et al.*)



Molecular model explains experimental results: Size effect a direct result of structural changes with profound impact on macroscale mechanical behavior

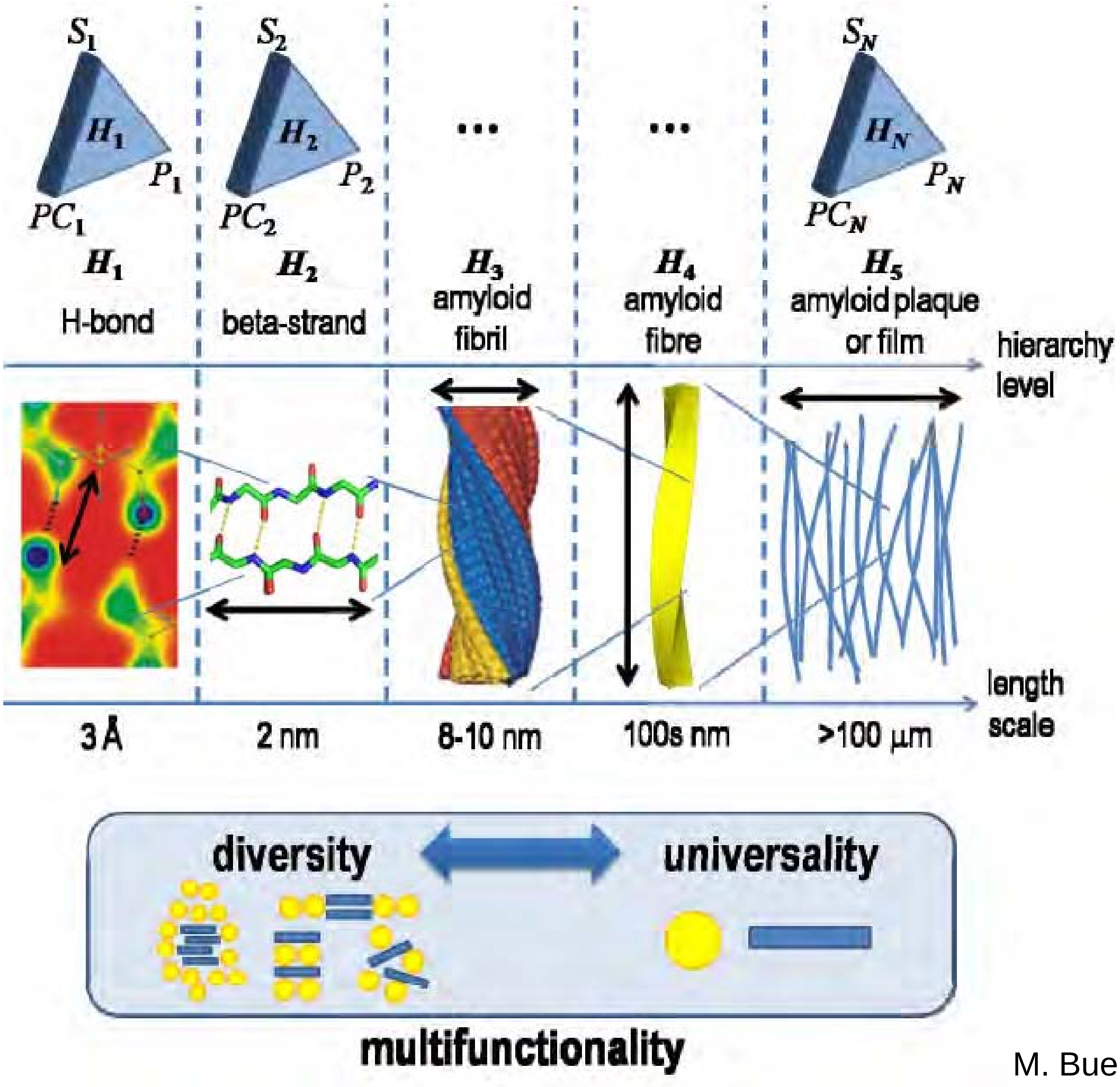
Keten, Nova, Buehler *et al., Nano Letters*, 2010; Nova *et al*., in preparation

Merger of structure and material



Buehler *et al.*, *Materials Today*, 2007

Universality and diversity (universality-diversity paradigm)

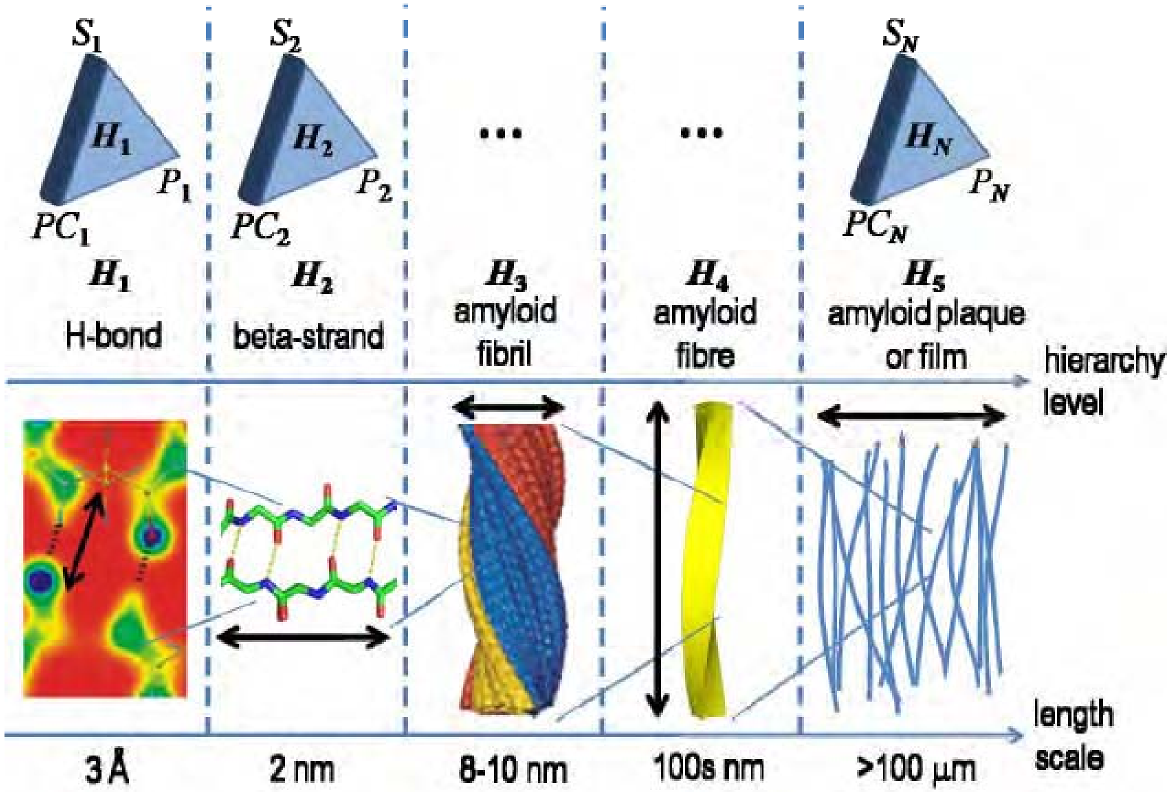


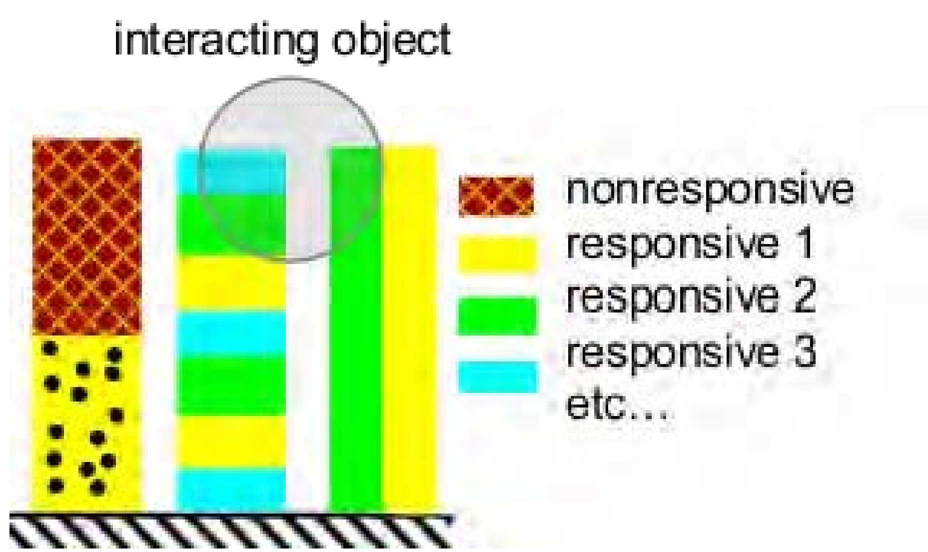
Create multifunctionality (diversity) by changing structural arrangements of few (universal) constituents rather than inventing new building blocks

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





… + other levels

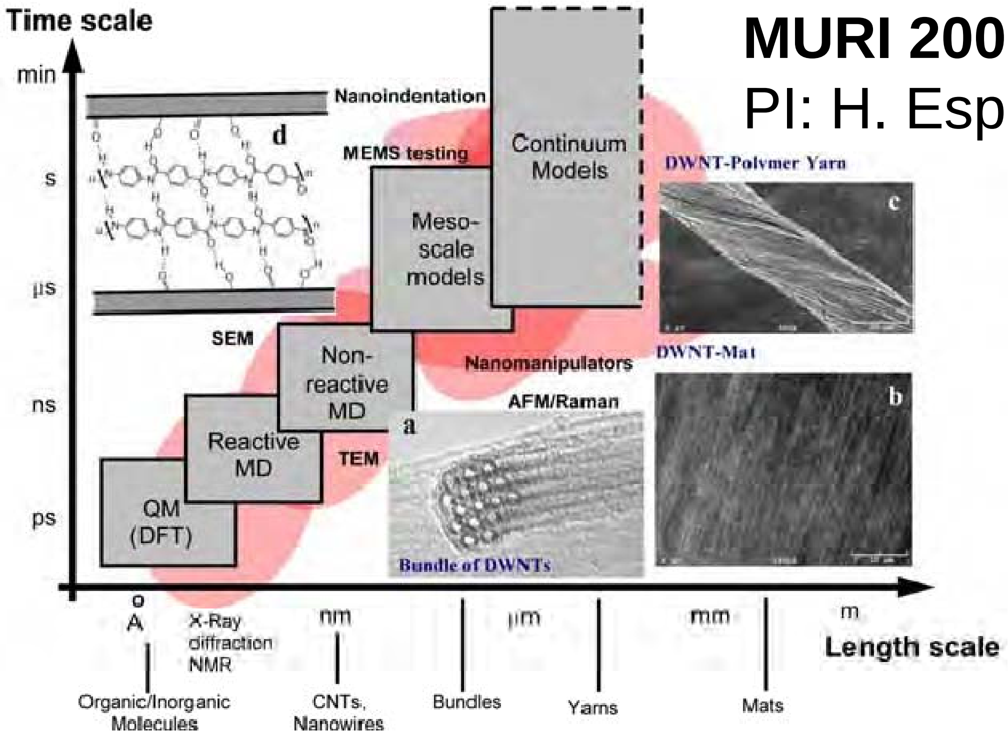
NSF-IRG
with C. Ortiz et al.

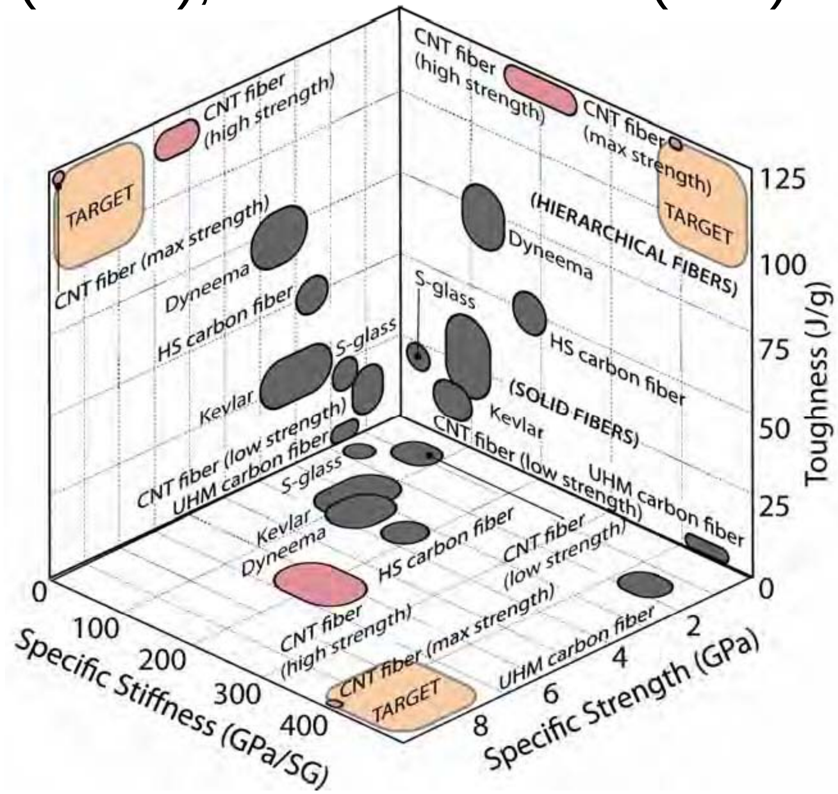
M. Buehler, *Nature Nanotechnology,* 2010

Practical impact: Transfer to synthetic fiber design based on nanomaterials

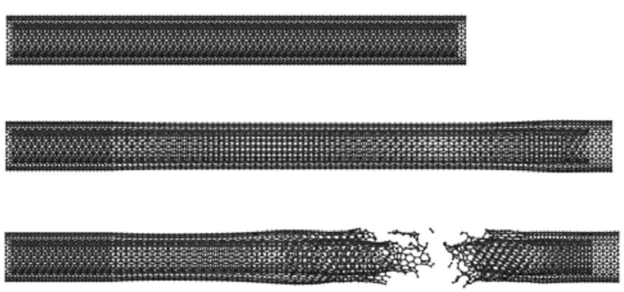
MURI 2009-2014 (ARO PM D. Stepp, D. Kiserow)

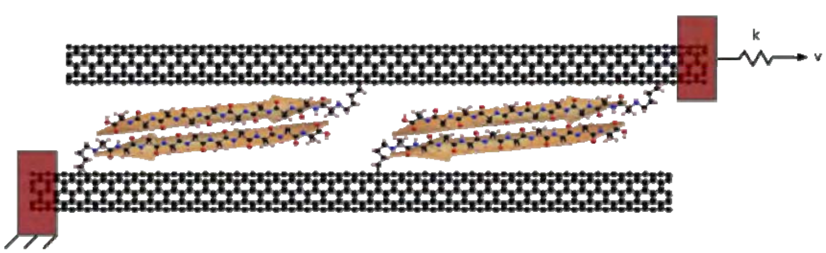
PI: H. Espinosa (NWU), with M. Buehler (MIT) *et al.*

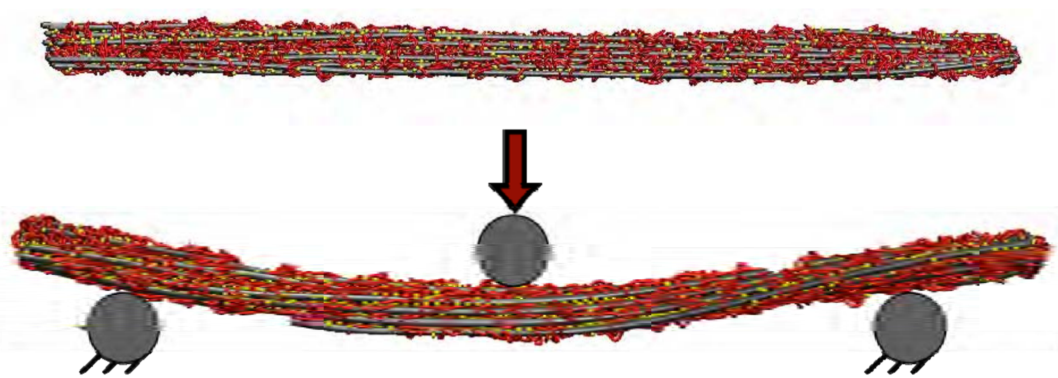




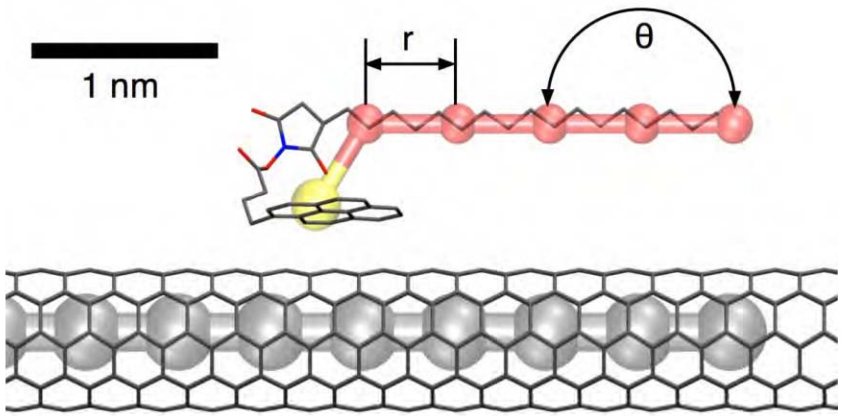
Results presented at MURI Kickoff Meeting, March 1 2010, Aberdeen, MD

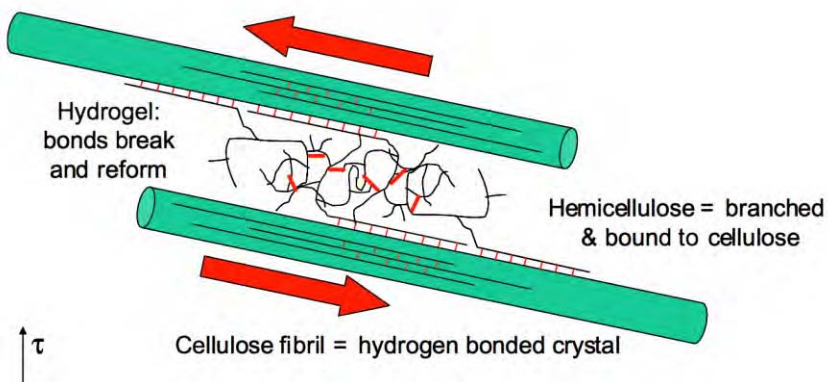


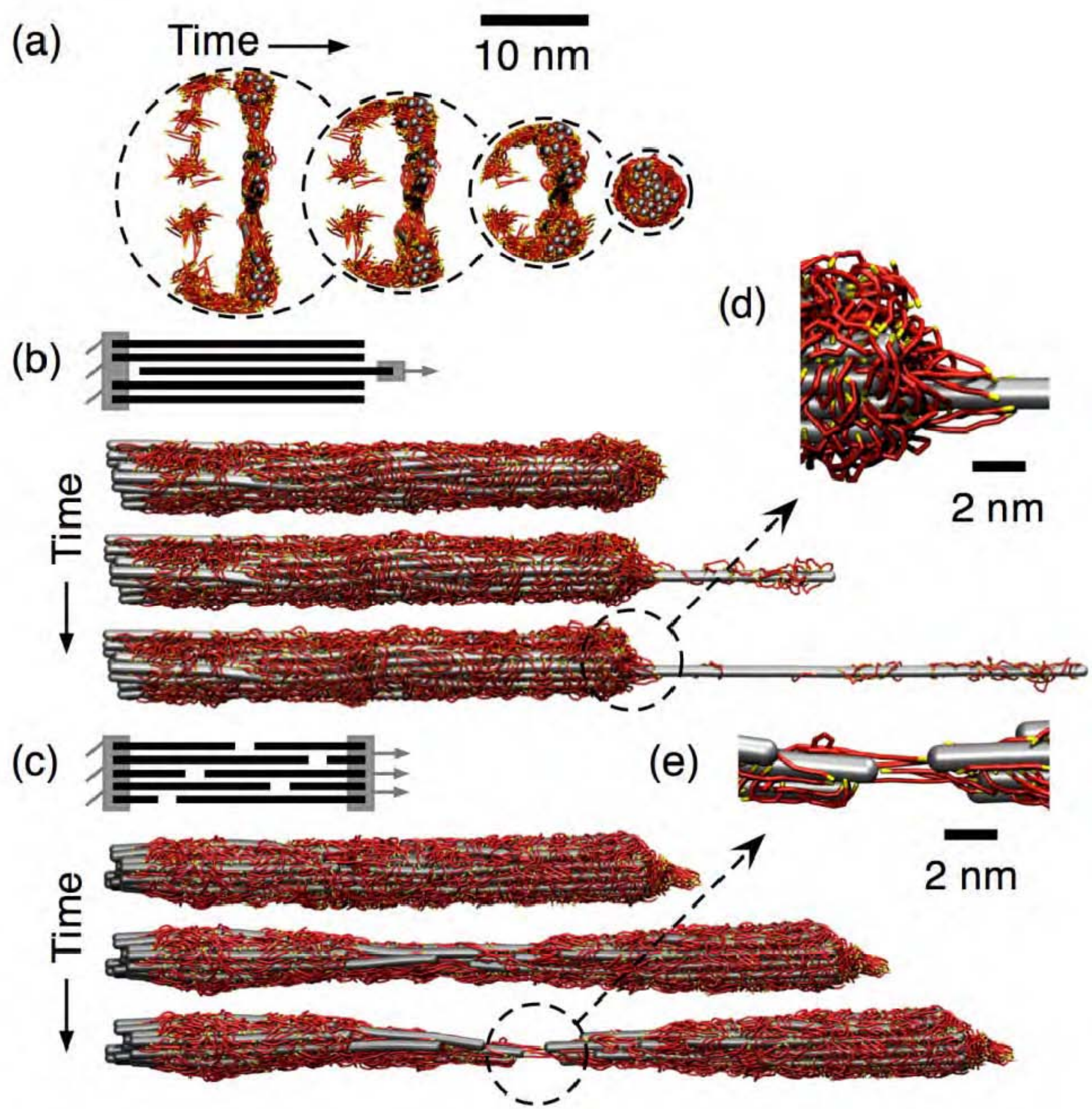




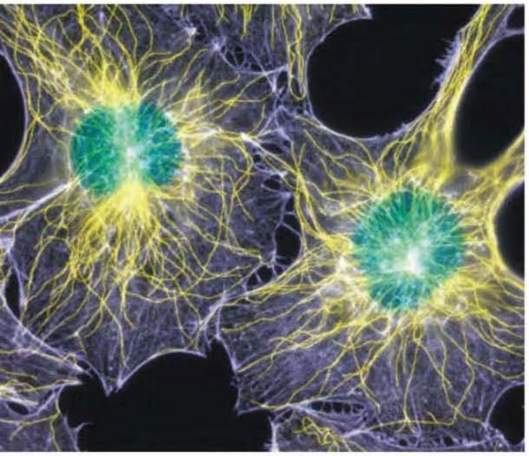
Wood-inspired CNT bundles

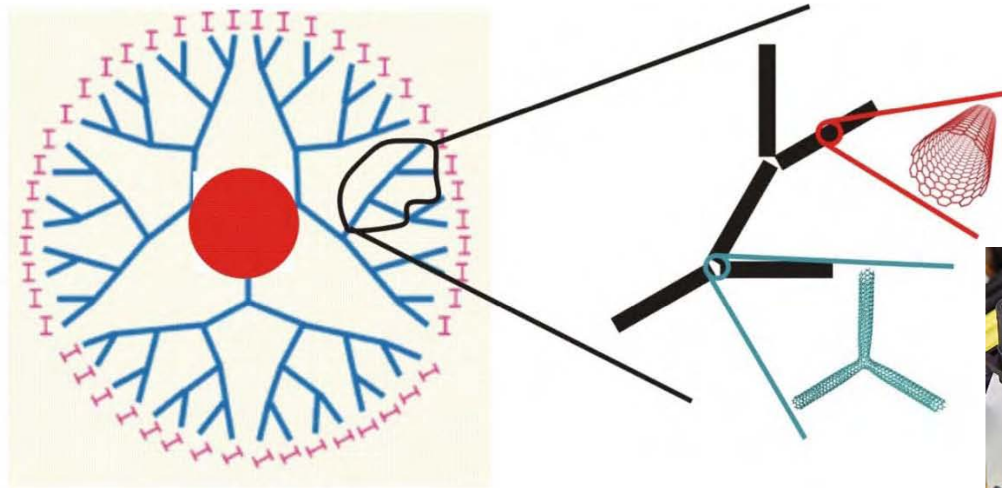




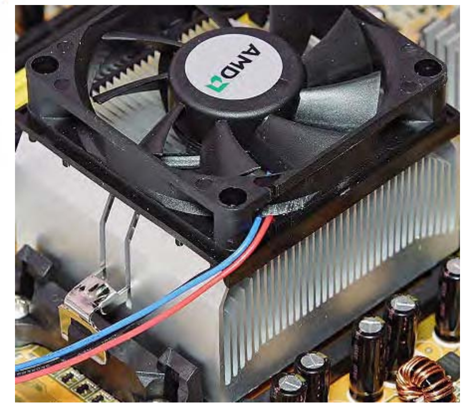


Bioinspired thermal materials



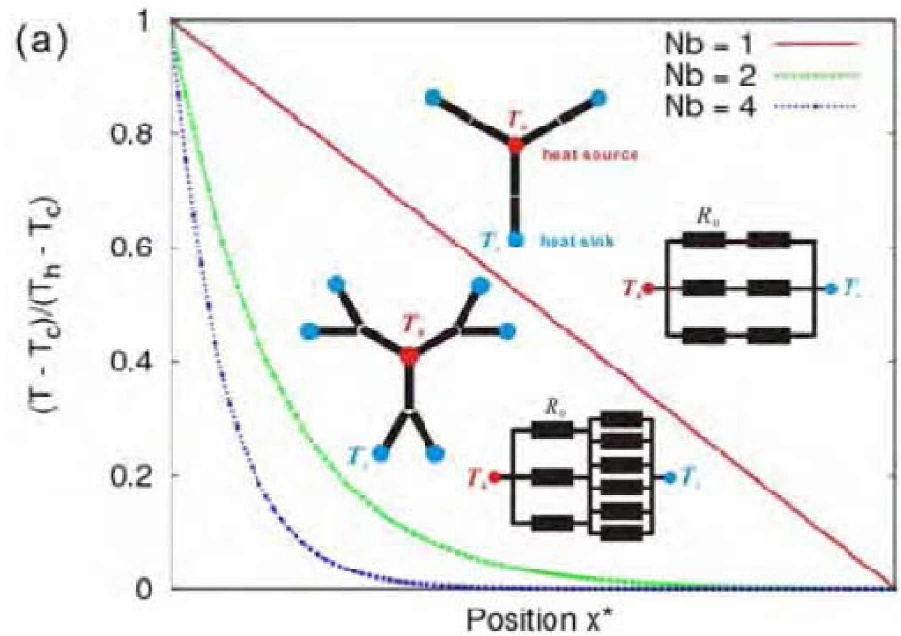


Funded by DARPA-MTO



heat source

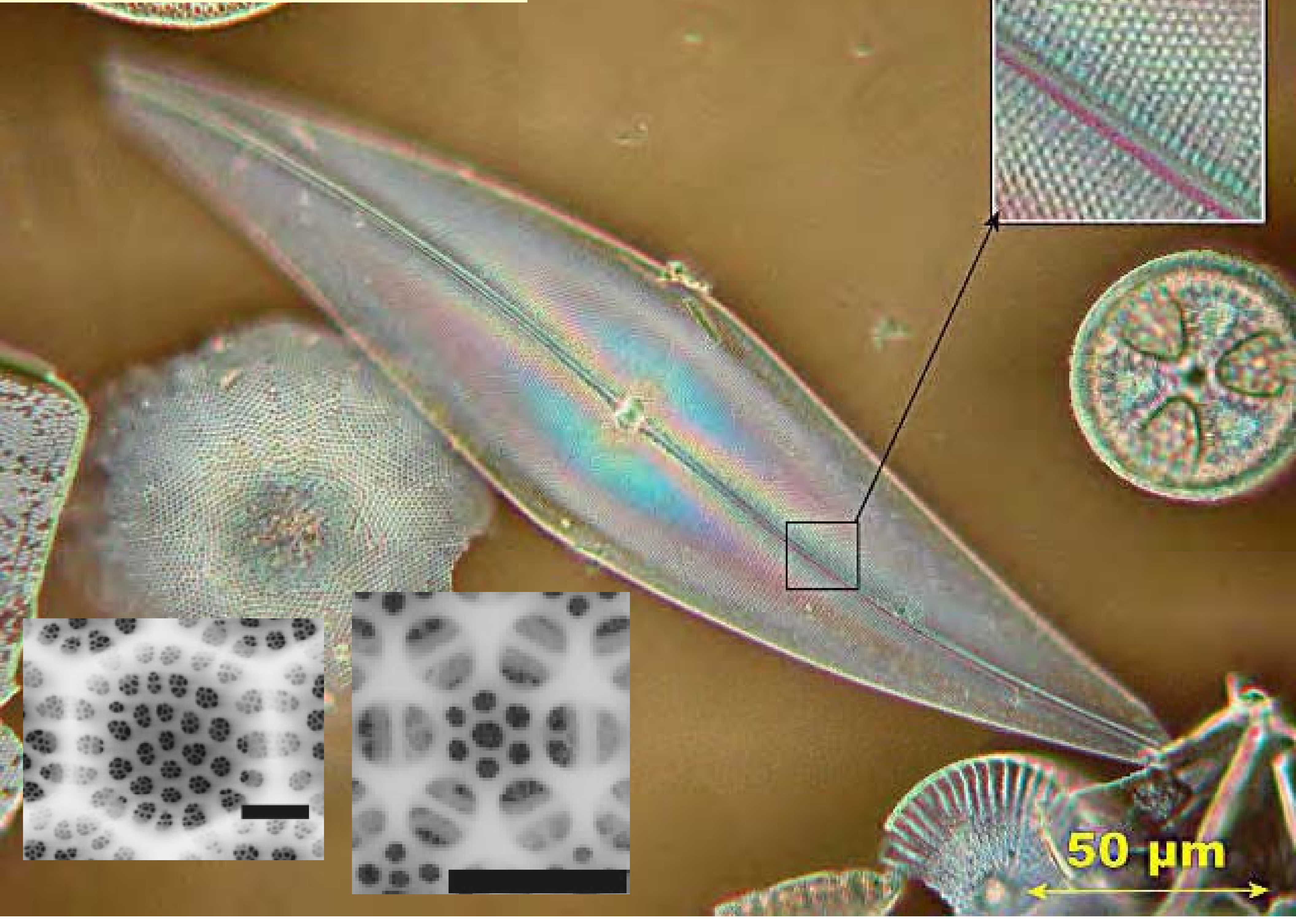
heat source



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

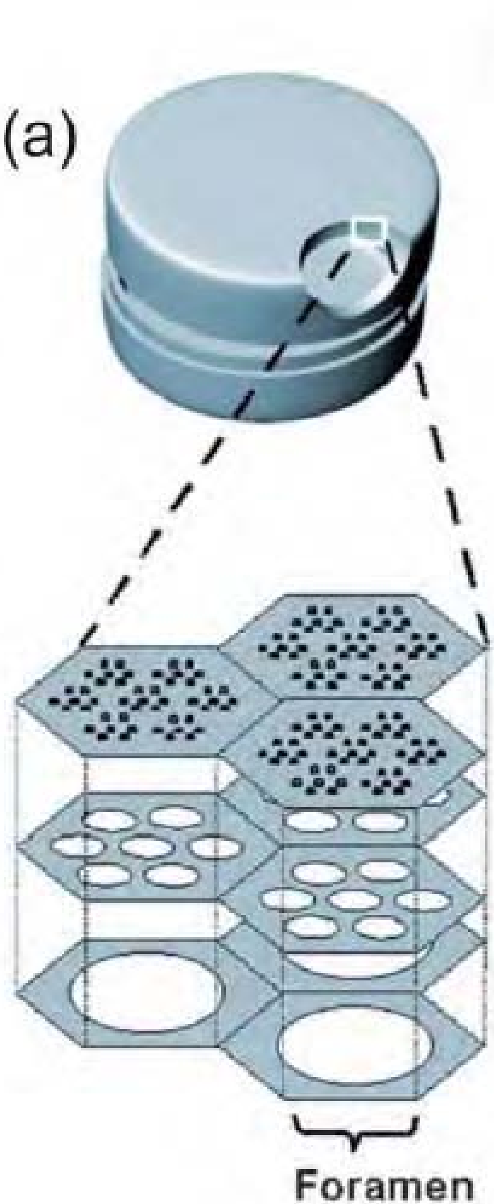
diatoms (silicified algae)

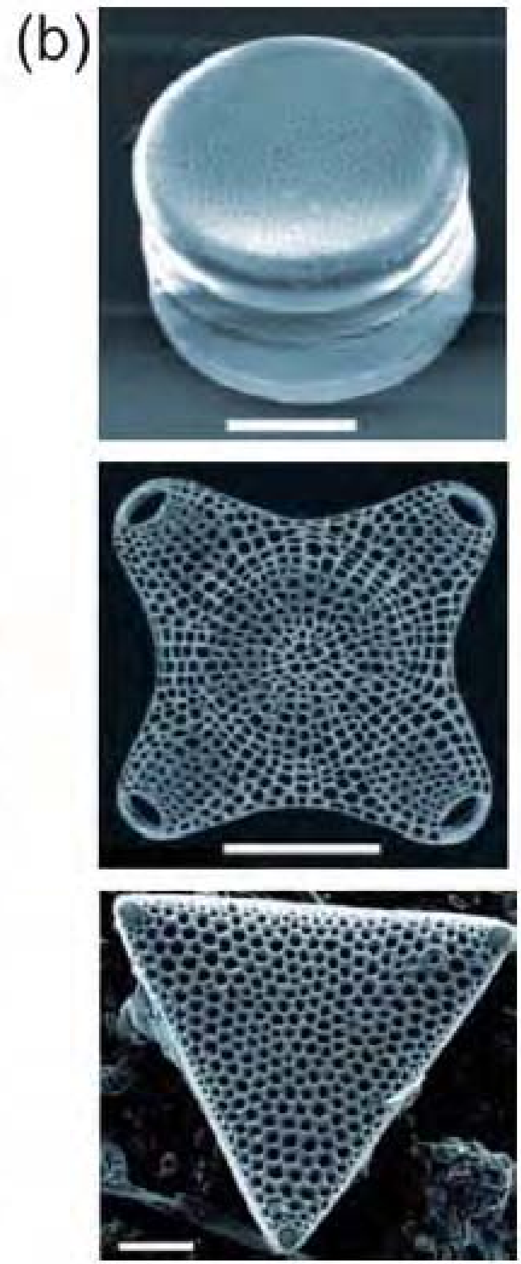


Hierarchical structure of sea sponges, diatoms

Hierarchical structure of diatoms, showing their porous silica structure

Garcia and Buehler, *COMMAT,* 2010

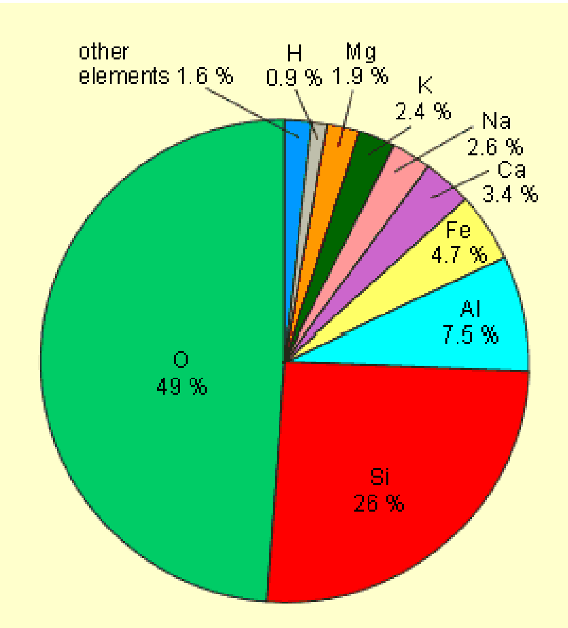




AFM and SEM images of various diatom species

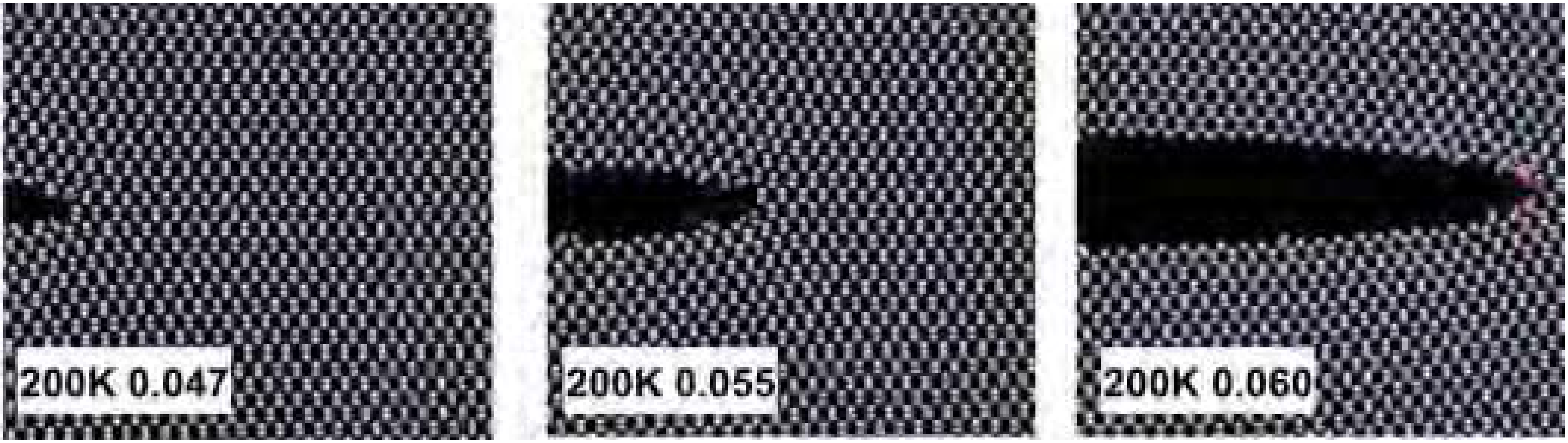
Losic *et al*. *Advanced Materials*, 2009

Silica and silicon is abundant, ***but brittle***



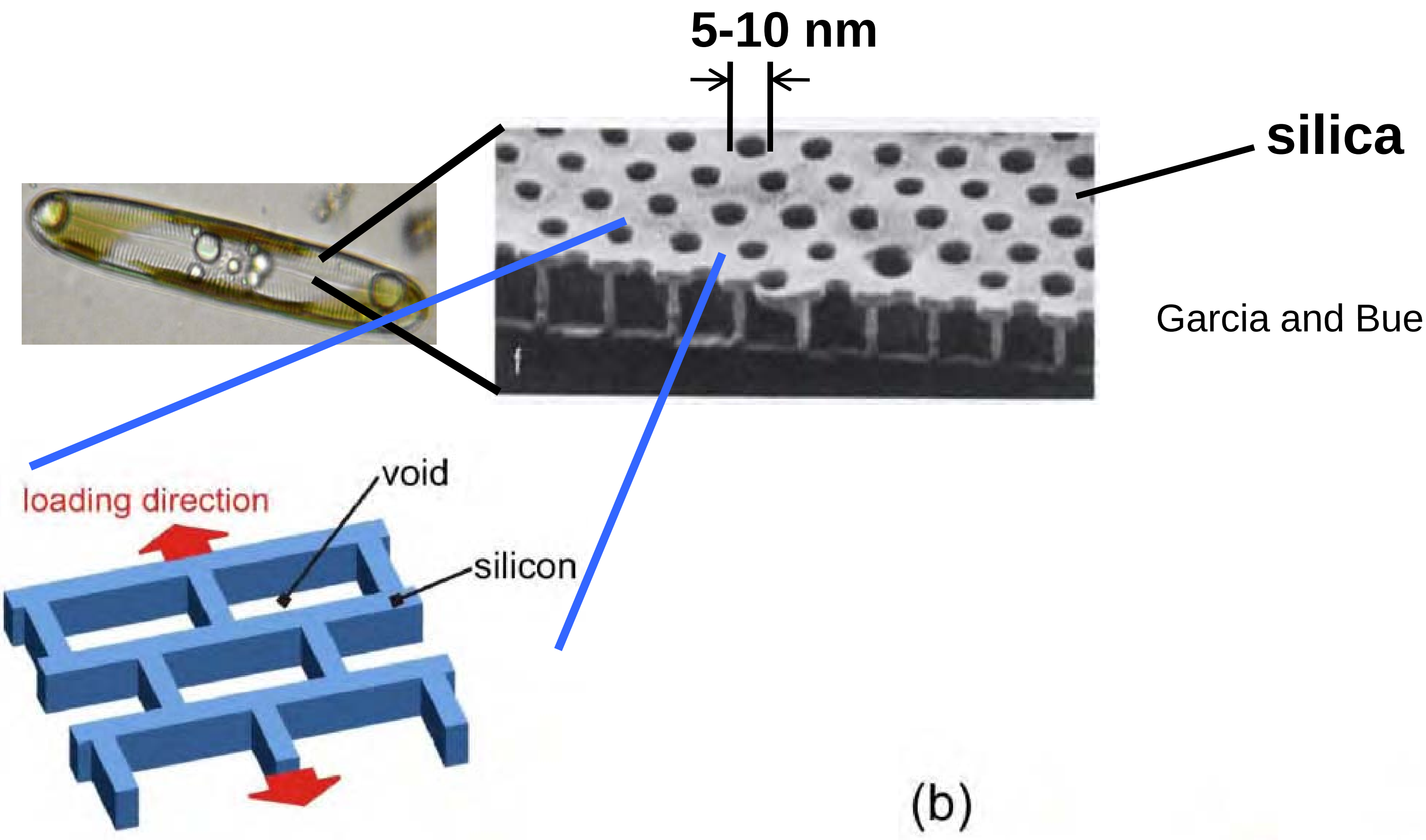
Silicon and oxygen – most abundant material in earth's crust

But – not useful as material (brittle)

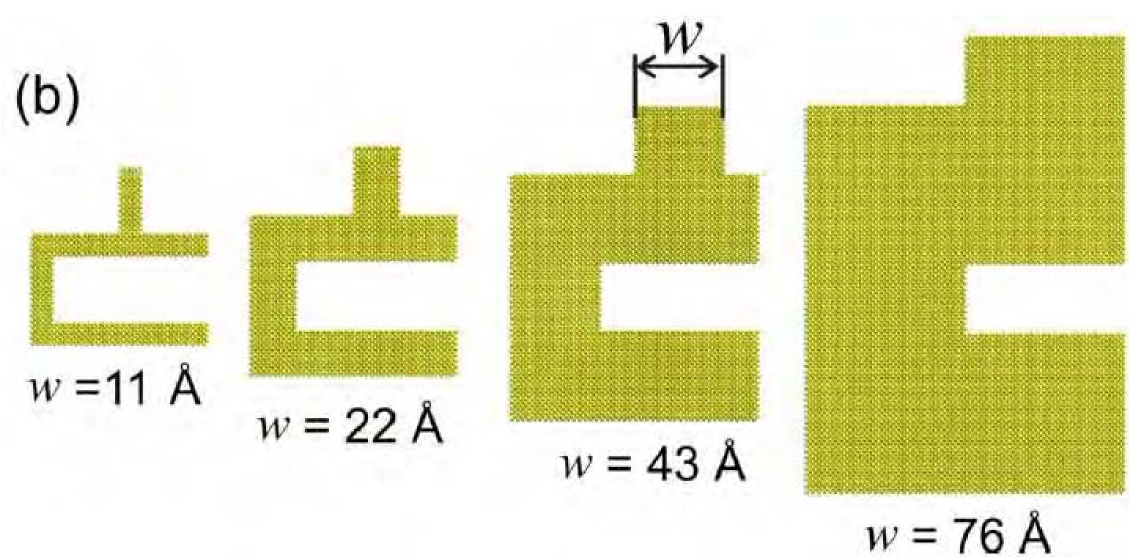


Sen, Buehler, *et al.*, *PRL*, 2010

Diatoms – Nature’s flexible armor



Garcia and Buehler, *COMMAT,* 2010

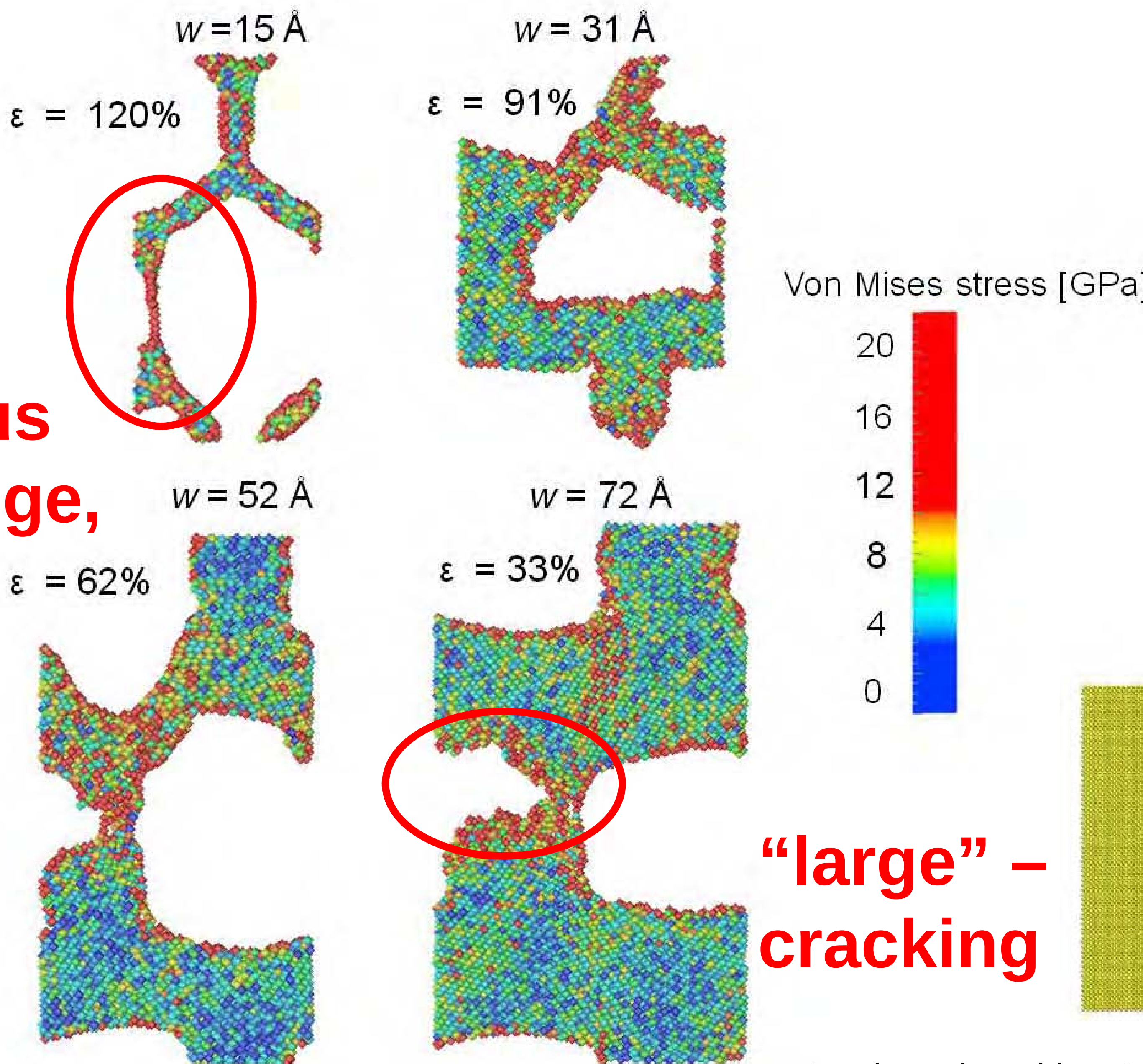


Model system to probe effects of nonporous structure on material performance

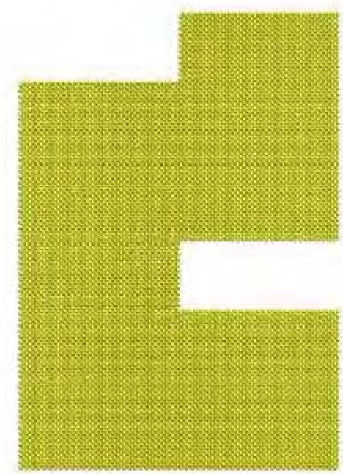
Controlled parameter width w

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)…

Summary, conclusion & discussion

- 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)