ERDC’s Advanced Materials Initiative – Using HPC Simulations to Develop Super Fibers and Super Ceramics
Materials Research from Nanoscale to Macroscale

Dr. Bob Welch
Co-Lead, ERDC Advanced Materials Initiative
Information Technology Laboratory
US Army Engineer Research and Development Center (ERDC)
Vicksburg, MS

Briefing to the 42nd HPC Users Forum
San Diego, California
7 September 2011
US Army Engineer Research and Development Center (ERDC)

2500 Employees

Over 1000 engineers and scientists
28% PhDs; 43% MS degrees

Research Laboratories of the Corps of Engineers

- Cold Regions Research Engineering Laboratory (Hanover, NH)
- Topographic Engineering Center (Alexandria, VA)
- Construction Engineering Research Laboratory (Champaign, IL)
- Headquarters (Vicksburg, MS)
- Coastal & Hydraulics Laboratory
- Environmental Laboratory
- Geotechnical & Structures Laboratory
- Information Technology Laboratory

Army “Research Lab of the Year” 4 of the past 5 years
ERDC Researchers: Dr. Bob Ebeling (Team Lead-Structural Concepts), Dr. Charles Marsh (Team Lead-Material Synthesis), Dr. Charles Cornwell (Team Lead – Atomistic Modeling), Dr. Mei Chandler, Toney Cummins, Dr. Paul Allison, Clint Arnett, Dr. N. Jabari Lee, Dr. James Baylot, Dr. Bryce Devine, Dr. Fran Hill, Thomas Carlson, Dr. Kevin Abraham, Pete Stynoski, Thomas Hymal, Jonathan George, Ben Ulmen, Dr. Meredith C.K. Sellers, Kyle Ford, Erik Wotring, Mr. Wayne Hodo, Dr. Jeff Allen, Dr. Laura Walizer

Natick Collaborators: Claudia Quigley, Karen Buehler, Dr. Mike Sennett

NASA Collaborators: Dr. Richard Jaffe (NASA Ames), Dr. Mike Meador (NASA Glenn)

Rice U. Collaborators: Prof. Matteo Pasquali, Nobel Laureate Prof. Robert Curl, Prof. Robert Hauge

DTRA Collaborators: Dr. Jeffrey DePriest, Dr. Heather Meeks

MIT/ISN Collaborators: Prof. Mike Strano, Prof. Markus Buehler

U. of Illinois/Champaign Collaborators: Prof. Parimita Mondal, Prof. Waltrude Kriven, Prof. Alexi Bezryadin

ARL Collaborators: Dr. Daphne Papas, Dr. Michelle Fleischman

ARO MURI Team Collaborators: Dr. David Stepp, Dr. Doug Kiserow, Northwestern U., others

Imperial College/Queen Mary College: Prof. Eduardo Saiz, Prof. Mike Reece (funded/coordinated through Army International Research Office, Dr. Steve Grant)

DoD HPCMO PETTT-funded Collaborators: Prof. Susan Sinnott (U. FL); Prof. Steve Stuart (Clemson U.); Prof. Anthony Rollett (Carnegie Mellon U.)

Program Managers – Dr. Bob Welch and Dr. John Peters
Development of materials has been largely empirically-based and has been largely evolutionary.

We, and others, are working to change the material development paradigm by employing several key technologies, attempting a manyfold improvement in material performance.

Our approach employs:
- Atomistic and multiscale simulations to guide material design and synthesis.
- Carbon nanotubes (CNTs) and other “super” molecules or crystals as strength members.
- Multiscale material response and diagnostic experiments to validate simulations.
- Advanced material synthesis.

*Design first, then build (at the molecular level).*
Initial Super Materials Program: Carbon Nanotube-Based Filaments, Membranes

Goal: Develop carbon nanotube (CNT)-based 1-million-psi tensile material (filaments, membranes) to Technology Readiness Level 4 (laboratory demo).

This would be a major accomplishment:

- Results in material with 2X strength/weight ratio of Kevlar and 5X tensile strength of very high strength steel (4340 alloy).
- Inaugurates a paradigm shift in material development.
- Lays the technical foundation for rapid development of other “super” materials and materials by design.
Carbon Nanotubes

Promise

- Carbon nanotubes (and graphene) are the strongest molecules ever discovered.
- Tensile strength of ~110 Gpa (15.5 million psi, 150 X high-strength steel).
- Density 1/6 to 1/3 that of steel (multiwall versus single-wall).
- Young’s modulus 1 TPa (150 million psi, 5 x that of steel).
- Strength/Weight Ratio – 450X to 900X steel.

Shortcomings

- Strength and stiffness properties exist only at the molecular level.
- Carbon nanotubes suffer brittle failure.
- Carbon nanotubes have weak intermolecular bonds.
- Carbon nanotubes are expensive (costs are falling dramatically).
Effects of Molecular Defects on CNT Tensile Strength

- CNTs display amazing strength and stiffness even with defects.
- Most carbon nanotubes suffer brittle failure at room temperature.
- Simulation results were substantiated in Peng et al., 2008.

Tight Binding Molecular Dynamics simulations of (5,5) carbon nanotubes

(Welch et al., 2006; Haskins et al., 2007)
Some ERDC Scientific Contributions from Molecular Dynamics Simulations

Defects and CNT tensile strength; brittle behavior of most CNTs (predicted Haskins et al., 2007; validated Peng et al., 2008)

MD Simulations Using Statistical Models of Molecular Constructs (Cornwell et al., 2009)

van der Waals forces are asymptotic
No critical length. (Cornwell et al., 2008)

Methods to overcome CNT brittle behavior by chirality and pre-twisting (Welch et al., 2006; Majure et al., submitted)
Interstitial Carbon Atom Bonding Between CNTS - Preliminary Results

- Experimentalists report interstitial carbon atom-CNT bonds created via irradiation (e.g., Kis et al., 2004; Peng et al., 2008).
- Interstitial carbon atom-CNT bonds are several orders of magnitude stronger than van der Waals forces.

Interstitial carbon atom-CNT bond versus van der Waals (Majure et al., 2008)
Million PSI, Scalable CNT Fiber Design (Cross-Linked Fibers)

Simulations were perhaps the first to identify a scalable molecular design, and predict mechanical properties, for a many-million-psi fiber.
Building the CNT Fiber
Some ERDC Contributions - CNT Material Synthesis

Discovery of CNT Forest Growth Termination Mechanism (with MIT/ISN)

CCVD Synthesis Refinements (3.5-mm CNT Forests, possibly DoD Record)

384,000 PSI CNT Fiber (with MIT/ISN)

Microbiology directed ssDNA Ligation of CNTs (Arnett et al., Langmuir, 2010), Patent Pending

Self-Assembled Tube Structure (SATS) Discovery
ERDC Cover Article
Marsh et al., Carbon, May 2011.
Building a Scalable, Cross-Linked 1-Million-PSI (Plus) CNT Fiber

ERDC vacuum system with argon plasma

- ERDC is performing radio frequency plasma optimization experiments at CERL, Champaign, IL.
- ERDC, in collaboration with Army Research Lab (Dr. Daphne Papas, Dr. Michelle Fleischman) is performing additional plasma irradiation experiments in Aberdeen.
- ERDC, in collaboration with U. of IL. (Prof. Bezryadin), is exploring metal infiltration for alternate cross-linking based strengthening methods and conductivity enhancement.
- Northwestern U. (Espinosa and Schatz Groups) leads a consortium that is using e-beam radiation to attempt to build a very strong scalable CNT fiber (ARO-funded MURI).
- Cambridge U. (Windle Group) is using e-beam irradiation to attempt to build very strong scalable CNT fiber (Natick and ONR funded).

ERDC, and others, are close to producing a lab demo of a scalable carbon nanotube fiber with a tensile strength of over 1-million psi.
ERDC Advanced Material Initiative

Super Ceramic
### Material Properties of Ceramics Compared with Those of Steel and Aluminum

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s Modulus (million psi)</th>
<th>Compressive Strength (ksi)</th>
<th>Density (lb/ft³)</th>
<th>Fracture Toughness (MPa m⁰.⁵)</th>
<th>Bending Strength (ksi)</th>
<th>Maximum Service Temp (F Degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon Carbide (SiC)</td>
<td>59.5</td>
<td>566</td>
<td>194</td>
<td>4.6</td>
<td>80</td>
<td>3000</td>
</tr>
<tr>
<td>Boron Carbide (B₄C)</td>
<td>63.8</td>
<td>560</td>
<td>157</td>
<td>3.1</td>
<td>62</td>
<td>1112</td>
</tr>
<tr>
<td>Aluminum Oxide (Al₂O₃)</td>
<td>43.5</td>
<td>305</td>
<td>230</td>
<td>3.5</td>
<td>47</td>
<td>3092</td>
</tr>
<tr>
<td>Very High Strength Steel (4340)</td>
<td>29.7</td>
<td>160 - 200</td>
<td>490</td>
<td>50</td>
<td>160 to 200</td>
<td>Melting Point - 2600</td>
</tr>
<tr>
<td>Aluminum 7075-T6</td>
<td>10.4</td>
<td>74 - 78</td>
<td>170</td>
<td>24</td>
<td>74-78</td>
<td>Melting Point – 900</td>
</tr>
</tbody>
</table>

- Ceramics have very high compressive strength and modulus.
- Ceramics are highly corrosive resistant and operate at very high temperatures.
- Silicon Carbide (SiC) has been mass produced since 1893.
- SiC is made from abundant materials (e.g., silicon sand and carbon).
- Ceramics have low tensile strength and fracture toughness (so does concrete).
Long-Term Goal: Super Ceramic

Development approach:

- Use silicon carbide (SiC) or other ceramic as matrix (compressive member).
- Employ CNTs or graphene for tensile strength/fracture toughness.
- Material design is similar to steel-reinforced concrete but at molecular scale.
- Experimentalists report 25% to 75% improvement in ceramic toughness via inclusion of CNTs, e.g., Xai et al., 2004; Wang, 2006; Karandikar, 2007; Yamamoto, 2008.
Super CNT/Graphene - Ceramic Composite

- Performance goals for CNT/graphene-ceramic composite are (5X tensile strength/toughness):
  - Density of ~175 lbs/ft³ – same as aluminum.
  - Min. Young’s modulus ~ 30 million psi – same as steel.
  - Min. compressive/tensile strength ~ 300,000 psi.
  - Min. fracture toughness – 25 MPa m¹/² - same as aluminum.

- Given the above, the CNT/graphene-SiC composite would have:
  - 3X stiffness-to-weight ratio of aluminum or steel.
  - 4X strength-to-weight ratio of high-strength aluminum (e.g., 7075-T6).
  - 9X strength-to-weight ratio of high-strength steel.

- CNT/graphene super ceramic would be made of carbon and silicon, abundant materials.

- CNT/graphene-SiC could result in 2/3 weight reduction (or more) for Army steel and aluminum equipment for designs constrained by maximum deflection or maximum load.

Warning: not known to be impossible, but considered very challenging goals. One ceramic researcher response: “not in my lifetime.”
Super Ceramic Impact on Army Logistics, Infrastructure- and Equipment-Weight Reduction

- Weight savings leads to additional weight savings.
- Lighter Army equipment leads to lowered requirements for bridging, air transport, and fuel.
- Lower fuel requirements lead to still lower logistics requirements.
- Super ceramic has major ramifications for DoD and U.S. economy (bridges, buildings, ships, planes, cars, trucks, etc).
Preliminary Simulations of Fracture in Nano-Crystalline 4H-SiC

- Columnar supercell of 20nm crystals viewed along the [1120] direction.
- Crystals are variously rotated around the [1120] axis. Stress is applied in the (1000) plane.
- Normal atoms are invisible for clarity.
- Black atoms are under-coordinated at grain boundaries and surfaces.
- Tan atoms are in a distorted crystal orientation (HCP instead of FCC).

(B. Devine, 2011)
National and Global Trends In Material Development
Molecular Design Approach to CNT Materials – What About Other Countries?

- Search on key words “carbon nanotubes” returned 45,000 hits:
  - U.S. – 9,600 articles
  - China – 9,100 articles
  - 59% of articles published since 2007.

- Search on “molecular dynamics” returned 120,000 hits:
  - U.S. – 30,100 articles
  - Japan – 12,400 articles
  - 56% of articles published since 2004.

- Search on “carbon nanotubes” and “molecular dynamics” returned 2392 articles:
  - U.S. – 647 articles
  - China – 456 articles
  - 55% of articles published since 2007.

Worldwide, other researchers are taking similar approaches. Most research occurred within last 4 years.
“Today, as part of his new Advanced Manufacturing Partnership, the President is announcing an ambitious plan, the Materials Genome Initiative, to double the speed with which we discover, develop, and manufacture new materials.... The President’s FY12 budget includes $100 million to launch the Materials Genome Initiative, with funding for the Department of Energy, the Department of Defense, the National Science Foundation, and the National Institute of Standards and Technology. The initiative will fund computational tools, software, new methods for material characterization, and the development of open standards and databases that will make the process of discovery and development of advanced materials faster, less expensive, and more predictable...”

“The lengthy time frame for materials to move from discovery to market is due in part to the continued reliance of materials research and development programs on scientific intuition and trial and error experimentation. Much of the design and testing of materials is currently performed through time-consuming and repetitive experiment and characterization loops. Some of these experiments could potentially be performed virtually with powerful and accurate computational tools...”

ERDC’s Advanced Materials Initiative has produced an early example of using atomistic computations to accelerate the development of an advanced material, a multi-million psi fiber, providing validation of the Materials Genome Initiative.
DARPA “Exascale” (Ubiquitous High Performance Computing) Program - Impact on Computation Materials Research

- DARPA Exascale Program goals: develop/demonstrate technologies to improve computing by 1000-fold across computing platforms by 2018.

- A few users will have access to top-end “ExaFlop” (1000 PetaFlop) machines.

- Other users are predicted to get 1000-fold improvement in their comparable machines.

- We use primarily DoD Supercomputing Resource Center (DSRC) at ERDC.

- ERDC-DSRC current capability is ~ 438 TFLOPS in 3 systems.
  - Cray XE6 (Garnet) – 20,160 cores, 194 TFLOPS - #51 (TOP 500 – June 2011)
  - SGI Altix ICE (Diamond) – 15,360 cores, 172 TFLOPS - # 48
  - Cray XT4 (Jade) – 8,584 cores, 72 TFLOPS - # 200

- Our typical large Molecular Dynamic (MD) simulations use ~ 2000 processors and 4-day compute (~0.2 million CPU hours).

- To gage Exascale Computing impact, we’ll assume a 1000-fold improvement.
Large Scale MD Simulations of SiC Sintering and Densification

- Sintering is used to manufacture polycrystalline SiC.
- Largest sintering simulations contain 20 million atoms and requires over $1.7 \times 10^5$ cpu hours (4-day compute).
- Simulations are limited to 20 nm crystals and 1 ns of time.
- Longer times are required for larger crystals to allow for comparable densification:
  - Rotation in smaller particles increases the number of low energy interfaces.
  - Increased fraction of higher energy surface atoms in smaller crystals.
- Exascale computing will allow simulation of 20-nm crystals and 1 micro-second of time (greater densification).
- Exascale computing will allow simulation of 100-nm crystals and 200 ns of time (extend crystal parameter space effects).

(B. Devine, 2011)
Large-Scale MD Simulations of Fracture in Columnar Nanocrystalline Silicon Carbide (SiC)

- 2D MD simulations reveal an effect on crystal size on fracture above 50 nm crystal size.
- 3D MD simulations are more representative.
- 3D model of 20-nm crystals contains 10 million atoms and is practical working limit (4-day compute, 0.2 million cpu hours).
- 3D models exploring effects above 50 nm are not practical.
- Exascale computing turns a 3D, 4-day computation into 6-minute computation, allowing SiC parameter space for strengthening and toughening to be explored quickly.
- Exascale computing allows 3D models up to 200 nm crystals (optimize crystal size).
- Exascale computing allows strain rates to be reduced by 1000 (better match to material experiments).

2D, 75-nm SiC crystalline structure under tensile loading
Exascale Computing – Effects on Computational Materials Science

- Exascale computing will increase the size and computational complexity of the material models resulting in more realistic physics-based simulations.

- Exascale computing will accelerate the trend for Molecular Dynamics simulations and materials experiments to operate at common length and time scales, allowing for greater verification and feedback between simulations and experiments.

- Exascale computing will further enable simulations to provide understanding of material response where experiments are impossible, dangerous, or too costly.

- Exascale computing will accelerate the trend for simulations to guide the design of materials and the methods of material manufacture.

- Exascale computing will accelerate material development.
The material development paradigm is changing (*design first; then build*):

- Atomistic/multiscale simulations used to guide material design.
- Exotic molecules/crystals, e.g., carbon nanotubes, silicon carbide.
- Evolving nanoscale diagnostics and experiments to validate simulations.
- Evolving synthesis methods.

ERDC and others are making rapid progress toward a multi-million-PSI CNT-fiber (lab demo) using these technologies.

ERDC is using these technologies to develop a ceramic composite to replace aluminum and steel with 2/3 weight reduction (lab demo).

The international community is adopting similar strategies towards material development with much of the work occurring within the last 4 years.

The President’s recent Material Genome Initiative strongly supports the acceleration of material development via the use of simulations.

DARPA’s Exascale Computing program will further enable simulation-based material development.

Revolutionary improvements in materials are occurring.
Engineering and Nanotechnology

We’ve reached the conclusion that many (most?) things that engineers care about are strongly influenced by phenomena at the nanoscale, for example:

Some macroengineering areas affected or controlled by nanoscale phenomena:

- Macromaterial strength & stiffness
- Friction
- Combustion and detonation
- Macromaterial synthesis
- Chemical properties
- Heat transmission
- Lubricants/coatings performance
- Photovoltaics
- Ice formation and adherence
- Corrosion, weathering, aging
- Fluid-structure interaction
- Electrical and magnetic material properties
- Cellular and subcellular behavior
- Life.

Nanotechnology is the big frontier for engineering technology advancement for the next several decades.
Building Molecular Dynamics (MD) Modeling Capabilities
Grain Boundary Simulations

Prescribed parameters in MD model build thus far:
1. Crystallographic orientation
2. Grain boundary thickness
3. Grain boundary composition
4. Grain boundary orientation (azimuthal & polar)
5. Fiber length and orientation (azimuthal & polar)
6. Fiber crosslink concentration (CNT-CNT & CNT-matrix)
7. Fiber average CNT length and standard deviation
Thank you.
Top 500 High-Performance Computational Resources
“The lengthy time frame for materials to move from discovery to market is due in part to the continued reliance of materials research and development programs on scientific intuition and trial and error experimentation. Much of the design and testing of materials is currently performed through time-consuming and repetitive experiment and characterization loops. Some of these experiments could potentially be performed virtually with powerful and accurate computational tools, but that level of accuracy in such simulations does not yet exist.”

ERDC’s Advanced Materials Initiative has produced an example of using atomistic computations to accelerate the development of an advanced material, a multi-million psi fiber, providing early validation of the Materials Genome Initiative.
Graphene has similar tensile strength/stiffness to that of CNTs and higher surface/mass ratio.

Preliminary nucleation simulation:

- Pristine graphene sheet (480 atoms) positioned near hot gas (1000 K to 2000 K) of 2000 Si and C atoms in 240 X 110 X 110 angstrom cell.

- Si and C atoms nucleate at graphene edges and at vacancies (1 ns simulation time).

- If SiC continued to grow, graphene would interleave and be covalently bonded to the SiC matrix.

- Increase tensile strength and fracture toughness?

*Note: Naval Research Lab recently grew graphene onto SiC substrate (Snow et al., February, 2011).*
Synthesizing CNTs
Modified Ferrocene Catalytic Chemical Vapor Deposition (CCVD)

- We started with minimal expertise in 2007.
- We adopted the CCVD method and further refined it to produce taller CNT forest (temperature, feed stock/carrier gas ratio, sonicator, etc.).
- We now grow CNT forests to 3.5 mm, possibly the record within the DoD.

Ferrocene CCVD Chamber
Synthesizing Ceramics: Developing ERDC Capability

- Down-selected Plasma Spark Sintering (SPS) as most promising (with Hot Press and Hot Isostatic Press as backups).
  - Collaboration with Imperial and Queen Mary Colleges (SPS, green forms).
  - Collaboration with ARL on SPS experiments (Dr. Jim Campbell).
- Testing advanced materials from St. Gobain, NanoAmor, XG Sciences, and NanoComp.
- Supporting MS and PhD theses at University of Illinois (Prof.s Kriven and Mondal).
  - Sintering study using liquid phase additive, HP/HIP approach, SPS transition.
  - Reinforced composite using SiO2 functionalized CNTs (SMART scholar).
- Developing predictive continuum sintering model (heat transfer, P, EM fields).
- Performing Molecular Dynamic (MD) simulations of nanocrystalline SiC sintering.
- Developing Potts mesoscale model for sintering (informed by MD simulations).
What is ERDC?
US Army Engineer Research and Development Center (ERDC)

2500 Employees

Over 1000 engineers and scientists
28% PhDs; 43% MS degrees

Cold Regions Research Engineering Laboratory (Hanover, NH)
Topographic Engineering Center (Alexandria, VA)
Construction Engineering Research Laboratory (Champaign, IL)
Headquarters (Vicksburg, MS)
Coastal & Hydraulics Laboratory
Environmental Laboratory
Geotechnical & Structures Laboratory
Information Technology Laboratory

Army “Research Lab of the Year” 4 of the past 5 years
Some of ERDC’s Unique Facilities

- DoD Supercomputer Center
  1 of 4 in DoD
- Hazardous & Toxic Waste Center
- Rapid Repair Levee Breach System
- Large-Scale Blast Simulation
- Large Hydraulic Models
- Ice Engineering
- Large Shaker Table (3-axis)
ERDC FY2011 Funding

- Armed Forces Support: 70%
- Civil Works: 20%
- Military Installations: 10%

Total Funding: $1.2 Billion
Environmental Risks of Nanomaterials

Do nanomaterials require special consideration of hazards because of their unique properties?

Dr. Jeffery A. Steevens, ST and Team Lead, Nanomaterials Risk, ERDC
Jeffery.A.Steevens@us.army.mil

Technical Team: Dr. Mark Chappell,
Dr. David Johnson, Dr. Amy Bednar,
Dr. Tony Bednar, Dr. Fran Hill,
Dr. Aimee Poda, Dr. Jacob Stanley,
Dr. Chuck Weiss, Chris Griggs,
Dr. Igor Linkov, Al Kennedy
Environmental Risk of Nanomaterials

- Materials Science
- Geochemistry and Colloid Science
- Toxicology
- Computational Chemistry
- Computer Science

Goal: Proactively support Army nanotechnology research and development
1. Determine **critical nanomaterial parameters** and mechanistic relationships regarding particle fate, transport, and toxicity.
2. Develop mechanistic and molecular models for **predicting environmental hazards and risks** of nanomaterials.
3. Use **life cycle approach** to enable acquisition process for delivering safe nanotechnologies to the soldier.
Nanomaterials Research

- Fundamental research
  - Fate; wide range of sizes (30-80 nm) and coatings; Behavior in biphasic systems (binding, agglomeration, stability)
  - Binding of nanoparticles to biotic surfaces resulting in toxicity
- NanoExPert™ Model for predicting hazards of nanoparticles
  - Database, fate model, toxicity estimates
- Life cycle risks
  - Releases and risks
  - Nanoaluminum energetics

Risk Assessment of Engineered Nanomaterials
http://el.erdc.usace.army.mil/nano/

Hyperspectral microscopy of biotic surfaces to support biotic ligand model

TEM of Nano aluminum developed for energetic and propellant, Tekna plasma system for nano Al synthesis, ARDEC