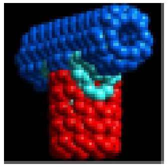
Ames Research Center

Nanotechnology: An Introduction and Overview



M. Meyyappan

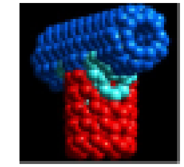
Center for Nanotechnology

NASA Ames Research Center

Moffett Field, CA 94035

email: m.meyyappan@nasa.gov

What is Nanotechnology?



Nanotechnology is the creation of **USEFUL/FUNCTIONAL** materials, devices and systems (of any useful size) through control/manipulation of matter on the nanometer length scale and exploitation of novel phenomena and properties which arise because of the nanometer length scale:

- Physical
- Chemical
- Electrical
- Mechanical
- Optical
- Magnetic

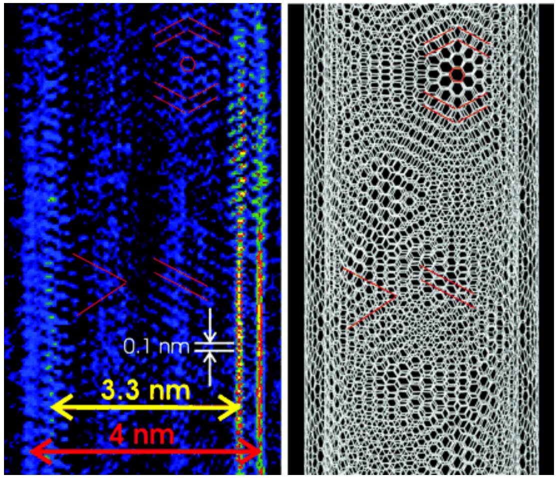
<u>Nanometer</u>

- One billionth (10^{-9}) of a meter
- Hydrogen atom 0.04 nm
- Proteins ~ 1-20 nm
- Feature size of computer chips 60 nm (in 2007)
- Diameter of human hair ~ 10 µm

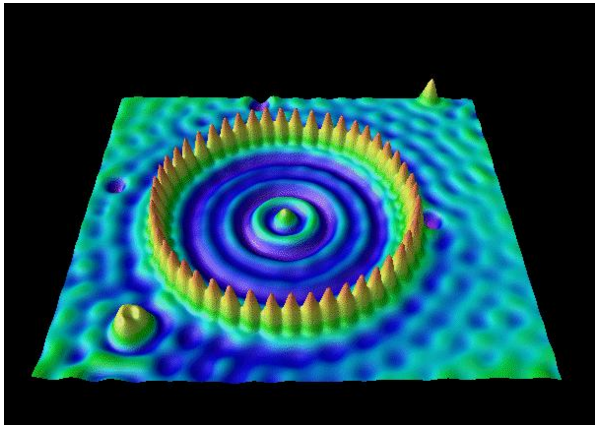
What Is Nanotechnology?

(Definition from the NNI)

- Research and technology development aimed to understand and control matter at dimensions of approximately 1 - 100 nanometer – the nanoscale
- Ability to understand, create, and use structures, devices and systems that have fundamentally new properties and functions because of their nanoscale structure
- Ability to image, measure, model, and manipulate matter on the nanoscale to exploit those properties and functions
- Ability to integrate those properties and functions into systems spanning from nano- to macro-scopic scales



Nanoarea Electron Diffraction of DW Carbon Nanotube – Zuo, et.al



Corral of Fe Atoms – D. Eigler

Source: Clayton Teague, NNI

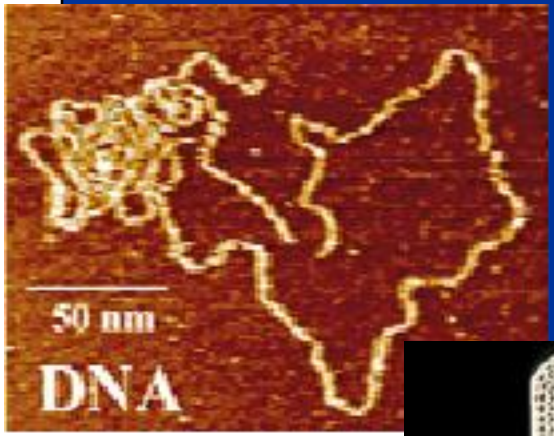
Examples of Nanostructures

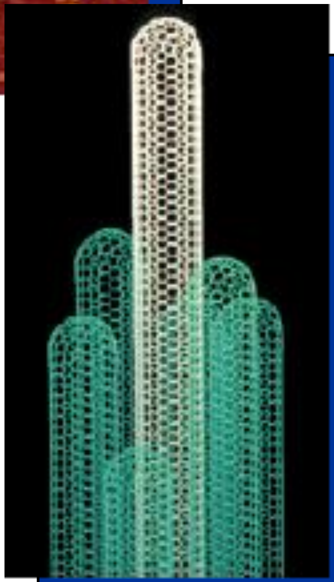
- Examples
  - Carbon Nanotubes
  - Proteins, DNA
  - Single electron transistors

- Not just size reduction but phenomena intrinsic to nanoscale
  - Size confinement
  - Dominance of interfacial phenomena
  - Quantum mechanics

- New behavior at nanoscale is not necessarily predictable from what we know at macroscale.

AFM Image of DNA

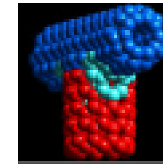




Unique Properties of Nanoscale Materials

- Quantum size effects result in unique mechanical, electronic, photonic, and magnetic properties of nanoscale materials
- Chemical reactivity of nanoscale materials greatly different from more macroscopic form, e.g., gold
- Vastly increased surface area per unit mass, e.g., upwards of 1000 m^2 per gram
- New chemical forms of common chemical elements, e.g., fullerenes, nanotubes of carbon, titanium oxide, zinc oxide, other layered compounds

Source: Clayton Teague, NNI

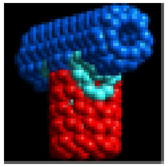


What is Special about Nanoscale?

- Atoms and molecules are generally less than a nm and we study them in chemistry. Condensed matter physics deals with solids with infinite array of bound atoms. Nanoscience deals with the in-between meso-world
- Quantum chemistry does not apply (although fundamental laws hold) and the systems are not large enough for classical laws of physics
- Size-dependent properties
- Surface to volume ratio
  - A 3 nm iron particle has 50% atoms on the surface
  - A 10 nm particle → 20% on the surface
  - A 30 nm particle → only 5% on the surface

Ames Research Center

What is new about Nanoscience?

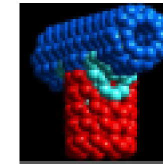


- Many existing technologies already depend on nanoscale materials and processes
  - photography, catalysts are “old” examples
  - developed empirically decades ago

- In existing technologies using nanomaterials/processes, role of nanoscale phenomena not understood until recently; serendipitous discoveries
  - with understanding comes opportunities for improvement

- Ability to design more complex systems in the future is ahead
  - designer material that is hard and strong but low weight
  - self-healing materials

Nano Revolution



STM

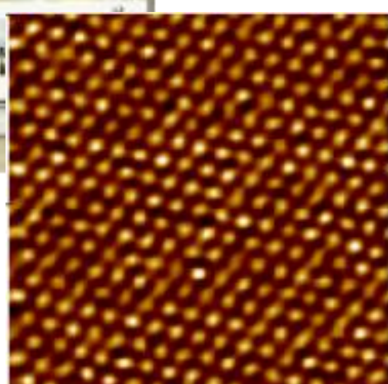


Image of Highly Oriented Pyrolitic Graphite

- 1959 Feynman Lecture *“There is Plenty of Room at the Bottom”* provided the vision of exciting new discoveries if one could fabricate materials/devices at the atomic/molecular scale.
- Emerging of instruments in the 1980s; STM, AFM providing the “eyes”, “fingers” for nanoscale manipulation, measurement…
- In the last decade, there has been an explosion of research on the nanoscale behavior of materials
  - Preparation of nanomaterials
  - Characterization and applications
  - Highly sophisticated computer simulations to enhance understanding as well as to create ‘designer materials’

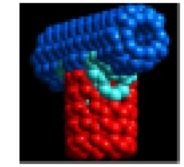
Ames Research Center

National Nanotechnology Initiative

- For information, www.nano.gov
- Multiagency Initiative in nanotechnology started in 2001 “National Nanotechnology Initiative (NNI) Leading to the Next Industrial Revolution”
- 2005 Nano budget was $1.0 Billion and similar funding level has been maintained since.
- Significant portion of the funding goes to NSF
  - Followed by DoD, DOE, NIH, and other Agencies
  - All these agencies spend most of their nano funding on university research programs
- Nano activities in U.S. companies: IBM, HP, Lucent, Hitachi USA, Lockheed Martin, Boeing, Corning, DOW, 3M…
  - In-house R & D
  - Funding of new ventures
- Nano Centers have been established at Universities all across the country
- Emerging small companies
  - VC funding

Ames Research Center

Initiatives in Other Countries



- Japan
- European Union
- Korea
- Taiwan
- Singapore
- China
- Israel
- Switzerland

Common Features

- Coordinated Government programs
- University R&D
- New Nano Centers
- Commercialization Focus
- Industry participation

NATIONAL NANOTECHNOLOGY INITIATIVE

NNI Program Component Areas (PCAs)

- Fundamental Nanoscale Phenomena and Processes
- Nanomaterials
- Nanoscale Devices and Systems
- Instrumentation Research, Metrology, and Standards for Nanotechnology
- Nanomanufacturing
- Major Research Facilities and Instrumentation Acquisition
- Societal Dimensions

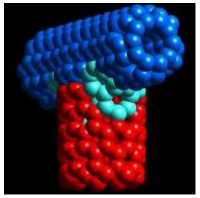
Source: Clayton Teague, NNI

Grand Coalition

- **Academia** will play key role in development of nanoscience and technology
  - Promote interdisciplinary work involving multiple departments
  - Develop new educational programs
  - Technology transfer to industry
- **Government Labs** will conduct mission oriented nanotechnology research
  - Provide large scale facilities and infrastructure for nanotechnology research
  - Technology transfer to industry
- **Government Funding Agencies** will provide research funding to academia, small business, and industry through the NNI and other programs (SBIR, STIR, ATP…)
- **Industry** will invest only when products are within 3-5 years
  - Maintain in-house research, sponsor precompetitive research
  - Sponsor technology start-ups and spin-offs
- **Venture Capital Community** will identify ideas with market potential and help to launch start-ups
- **Professional societies** should establish interdisciplinary forum for exchange of information; reach out to international community; offer continuing education courses

Ames Research Center

Nanotechnology R & D



Organic

Inorganic

Bio

Nanoelectronics and Related

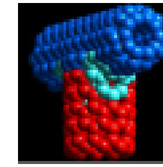
Sensors, NEMS

Structural Applications

Nanomaterials

Applications

Various Nanomaterials and Nanotechnologies

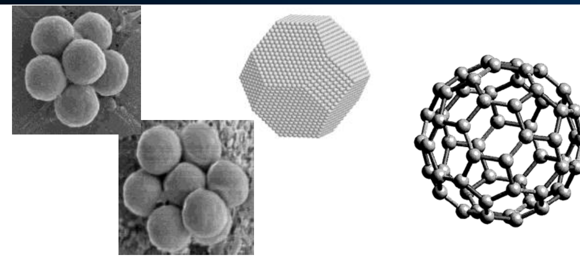


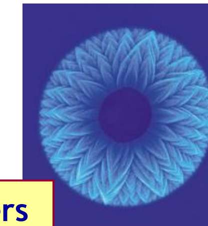
- Nanocrystalline materials
- Nanoparticles
- Nanocapsules
- Nanoporous materials
- Nanofibers
- Nanowires
- Fullerenes
- Nanotubes
- Nanosprings
- Nanobelts
- Dendrimers

- Nanoelectronics
- Quantum dots
- NEMS, Nanofluidics
- Nanophotonics, Nano-optics
- Nanomagnetics
- Nanofabrication
- Nanolithography
- Nanomanufacturing
- Nanomedicine
- Nano-bio

Extraordinary "Space" of Nanomaterials

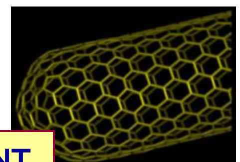
- Atom clusters





SiC Flowers

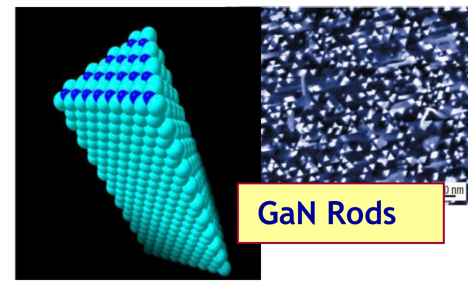
- Nanotubes, rods, spheres, belts … – carbon and other materials
- Dendrimers



C SWNT

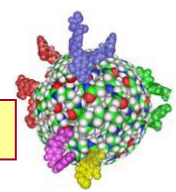
ZnO Belt

ZnO Tube

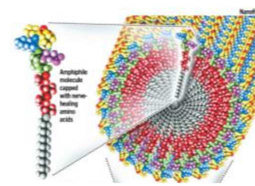


GaN Rods

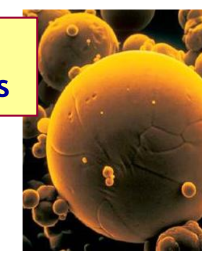
- Macro-molecular structures



Spherical



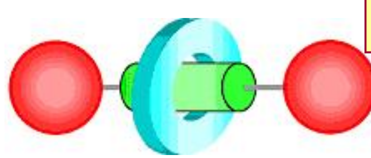
Tubular



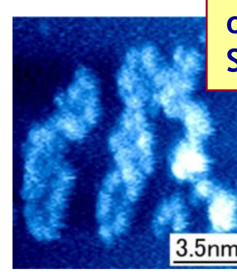
TiO_2 Spheres

- Biomolecular structures

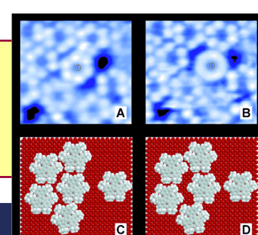
Catenane



Rotaxane



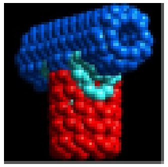
STM Image of DNA Segment



STM Image and Model of Porphyrin

Source: Clayton Teague, NNI

R & D Categories for Investment



As Recommended by the IWGN (Interagency Working Group on Nanotechnology) Panel

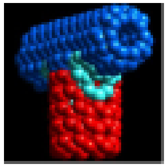
See www.nano.gov

- Nanostructure Properties
  - Biological, chemical, electronic, magnetic, optical, structural…
- Synthesis and Processing
  - Enable atomic and molecular control of material building blocks
  - Bioinspired, multifunctional, adaptive structures
  - Affordability at commercial levels
- Characterization and manipulation
  - New experimental tools to measure, control
  - New standards of measurement
- Modeling and simulation
- Device and System Concepts
  - Stimulate innovative applications to new technologies
- Application Development

Ames Research Center

Some Fundamental Science Issues

(As raised in the IWGN Report)

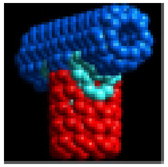


1. What novel quantum properties will be enabled by nanostructures (at room temp.)?
2. How different from bulk behavior?
3. What are the surface reconstructions and rearrangements of atoms in nanocrystals?
4. Can carbon nanotubes of specified length and helicity be synthesized as pure species? Heterojunctions in 1-D?
5. What new insights can we gain about polymer, biological…systems from the capability to examine single-molecule properties?
6. How can one use parallel self-assembly techniques to control relative arrangements of nanoscale components according to predesigned sequence?
7. Are there processes leading to economic preparation of nanostructures with control of size, shape… for applications?

This is NOT an exhaustive list

Ames Research Center

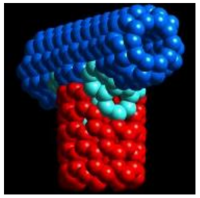
Some 'Nano' Definitions

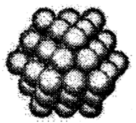
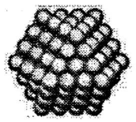
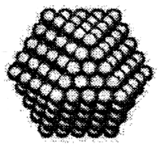
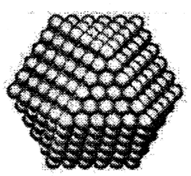
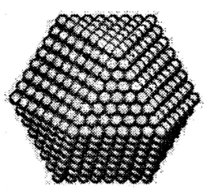


- Cluster
  - A collection of units (atoms or reactive molecules) of up to about 50 units
- Colloids
  - A stable liquid phase containing particles in the 1-1000 nm range. A colloid particle is one such 1-1000 nm particle
- Nanoparticle
  - A solid particle in the 1-100 nm range that could be noncrystalline, an aggregate of crystallites or a single crystallite
- Nanocrystal
  - A solid particle that is a single crystal in the nanometer range

Ames Research Center

Percentage of Surface Atoms

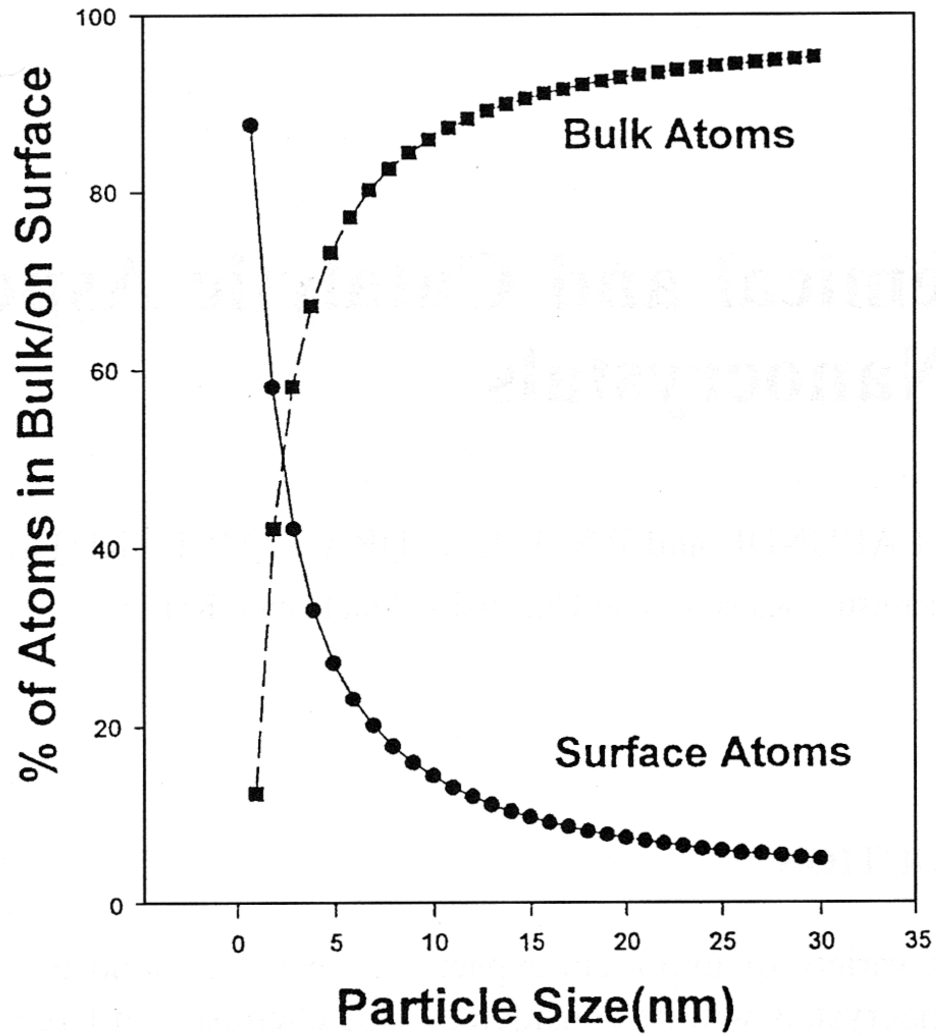


Full-shell Clusters		Total Number of Atoms	Surface Atoms (%)
1 Shell		13	92
2 Shells		55	76
3 Shells		147	63
4 Shells		309	52
5 Shells		561	45
7 Shells		1415	35

Source: Nanoscale Materials in Chemistry, Ed. K.J. Klabunde, Wiley, 2001

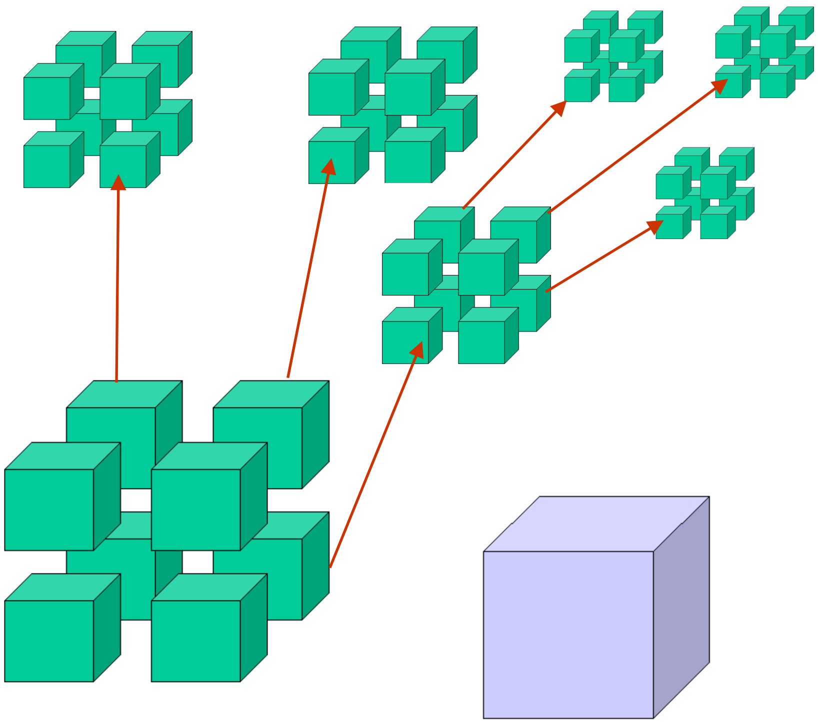
Surface to Bulk Atom Ratio

- Spherical iron nanocrystals
- J. Phys. Chem. 1996, Vol. 100, p. 12142



Nanoscale = High Ratio of Surface Area to Vol.

Repeat 24 times



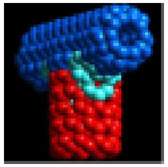
8 Cubes Side L
Each has Surface area $6L^2$
Total Surface Area 48 L^2

1 Cube
Length of sides 2L
Surface area 24 L^2

For example, 5 cubic centimeters - about 1.7 cm per side - of material divided 24 times will produce 1 nanometer cubes and spread in a single layer could cover a football field

Source: Clayton Teague, NNI

Size Dependence of Properties

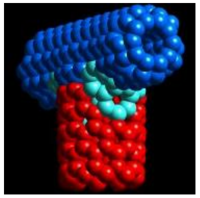


- In materials where strong chemical bonding is present, delocalization of valence electrons can be extensive. The extent of delocalization can vary with the size of the system.

- Structure also changes with size.

- The above two changes can lead to different physical and chemical properties, **depending on size**
    - Optical properties
    - Bandgap
    - Melting point
    - Specific heat
    - Surface reactivity
    -
    -
- Even when such nanoparticles are consolidated into macroscale solids, new properties of bulk materials are possible.
    - Example: enhanced plasticity

Some More Size-Dependent Properties



- For semiconductors such as ZnO, CdS, and Si, the bandgap changes with size
  - Bandgap is the energy needed to promote an ellectron from the valence to the conduction band
  - When the bandgaps lie in the visible spectrum, a change in bandgap with size means a change in color
- For magnetic materials such as Fe, Co, Ni, Fe_3O_4, etc., magnetic properties are size dependent
  - The 'coercive force' (or magnetic memory) needed to reverse an internal magnetic field within the particle is size dependent
  - The strength of a particle's internal magnetic field can be size dependent

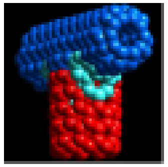
Color

- In a classical sense, color is caused by the partial absorption of light by electrons in matter, resulting in the visibility of the complementary part of the light
- On most smooth metal surfaces, light is totally reflected by the high density of electrons ⇒ no color, just a mirror-like appearance.
- Small particles absorb, leading to some color. This is a size dependent property.

  <u>Example</u>: Gold, which readily forms nanoparticles but not easily oxidized, exhibits different colors depending on particle size.

  - Gold colloids have been used to color glasses since early days of glass making. Ruby-glass contains finely dispersed gold-colloids.
  - Silver and copper also give attractive colors

Specific Heat



- $C = \Delta Q/m\Delta T$
  Specific heat is the amount of heat ΔQ required to raise the temperature by ΔT of a sample of mass m

- Units are J/kg ·K or cal/g ·K

- 1 calorie is the heat needed to raise the temperature of 1 g of water by 1 degree.

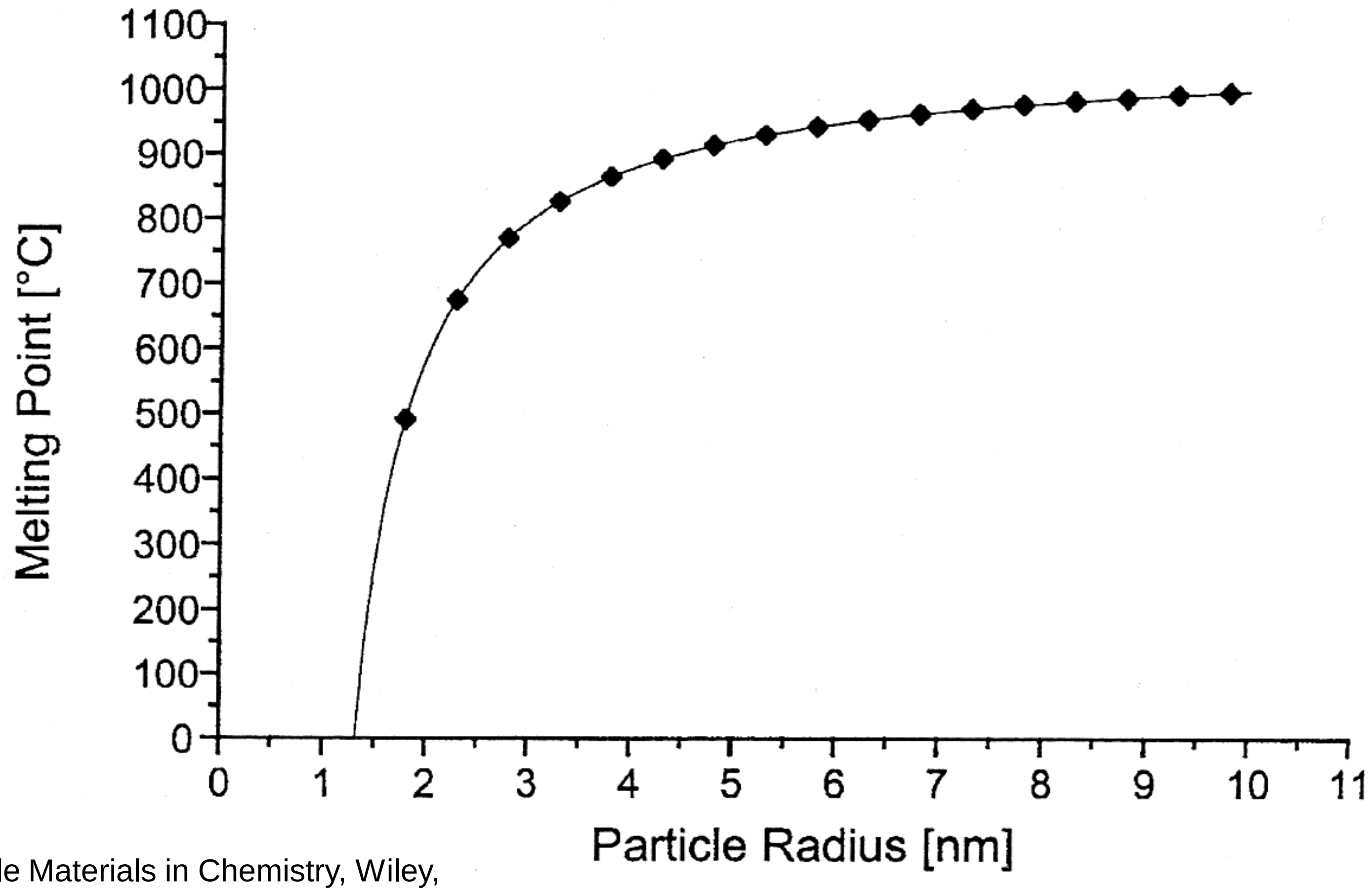
Specific Heat (cont.)

- Specific heat of polycrystalline materials is given by Dulong-Petit law
  - C of solids at room temp. (in J/kg ·K) differs widely from one to another; but the molar values (in J/moles ·k) are nearly the same, approaching 26 J/mol ·K; $C_v = 3\ Rg/M$ where M is molecular weight

- C_v of nanocrystalline materials are higher than their bulk counterparts. Example:
  - Pd: 48% ↑ from 25 to 37 J/mol.K at 250 K for 6 nm crystalline
  - Cu: 8.3% ↑ from 24 to 26 J/mol.K at 250 K for 8 nm
  - Ru: 22% ↑ from 23 to 28 J/mol.K at 250 K for 6 nm

Melting Point

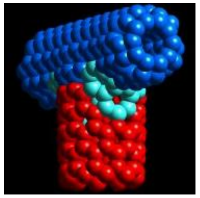
The melting point of gold particles decreases dramatically as the particle size gets below 5 nm



Source: Nanoscale Materials in Chemistry, Wiley,

Ames Research Center

Melting Point Dependence on Particle Size: Analytical Derivation



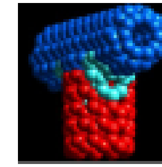
- Start from an energy balance; assume the change in internal energy (ΔU) and change in entropy per unit mass during melting are independent of temperature

$$\Delta\theta = 2T_o\sigma/\rho L r$$

$\Delta\theta$	=	Deviation of melting point from the bulk value
T_o	=	Bulk melting point
σ	=	Surface tension coefficient for a liquid-solid interface
ρ	=	Particle density
r	=	Particle radius
L	=	Latent heat of fusion

Ames Research Center

Electrical Conductivity



- For metals, conductivity is based on their band structure. If the conduction band is only partially occupied by electrons, they can move in all directions without resistance (provided there is a perfect metallic crystal lattice). They are not scattered by the regular building blocks, due to the wave character of the electrons.

$$\mu = \frac{e\lambda}{4\pi\varepsilon_o m_e v}$$

v = electron speed

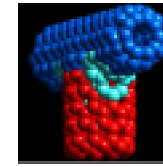
ε_o = dielectric constant in vacuum

τ, mean time between collisions, is λ/v

- For Cu, $v = 1.6 \times 10^6$ m/s at room temp.; $\lambda = 43$ nm, $\tau = 2.7 \times 10^{-14}$s

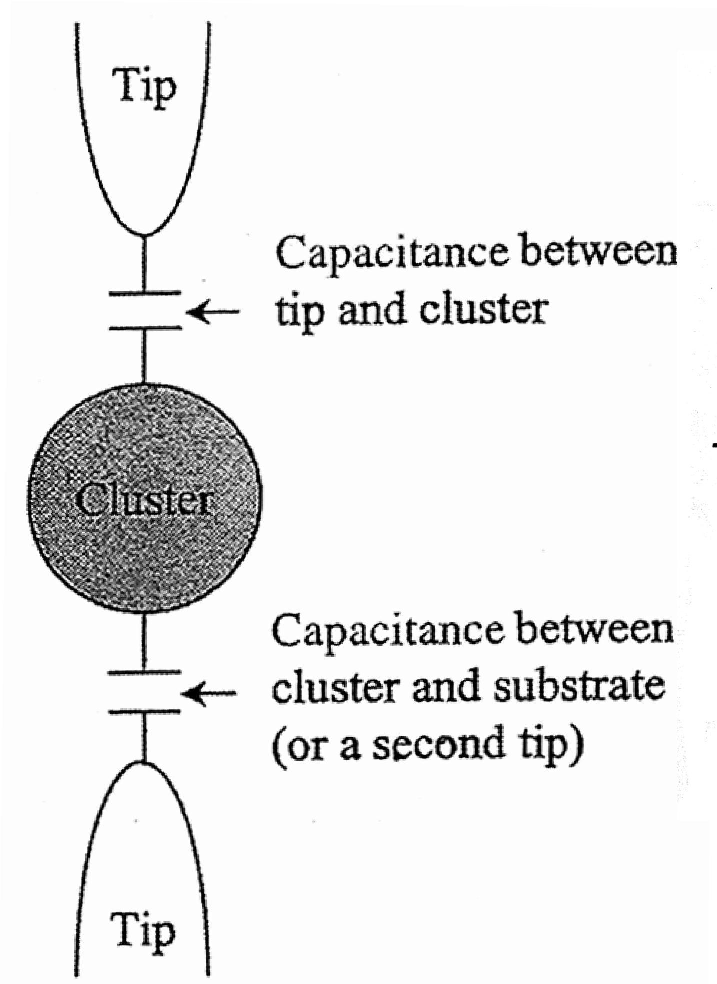
Ames Research Center

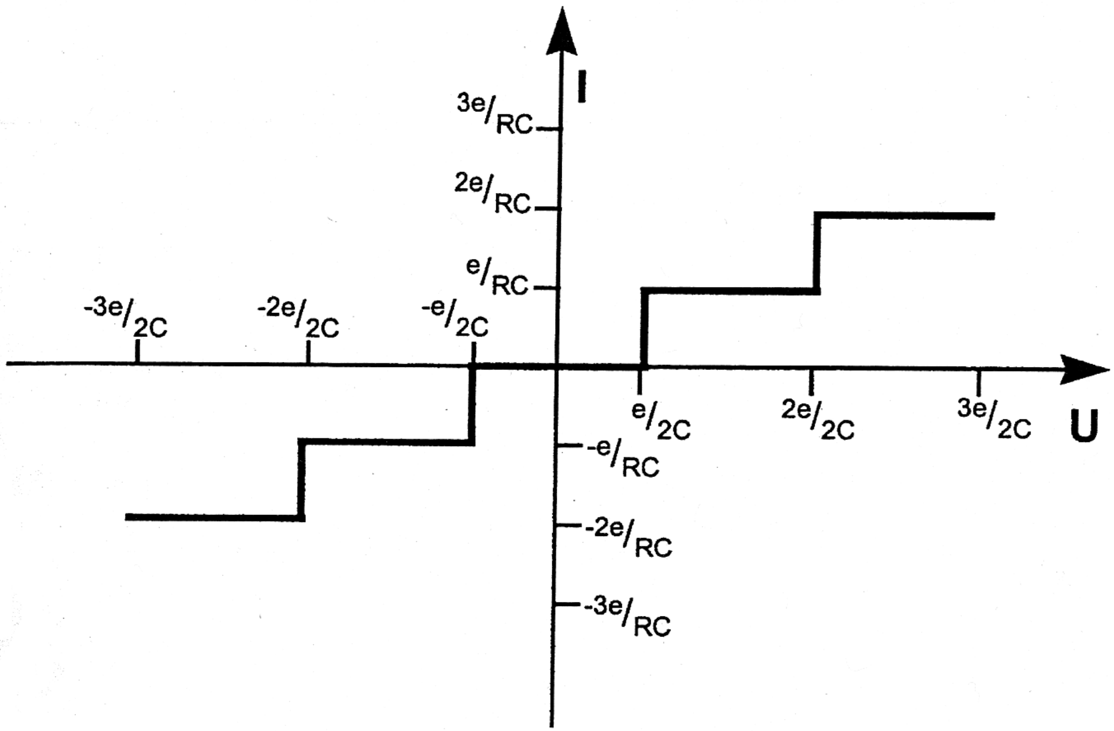
Electrical Conductivity (continued)



- Scattering mechanisms
  - (1) By lattice defects (foreign atoms, vacancies, interstitial positions, grain boundaries, dislocations, stacking disasters
  - (2) Scattering at thermal vibration of the lattice (phonons)
- Item (1) is more or less independent of temperature while item #2 is independent of lattice defects, but dependent on temperature.
- Electric current $\Rightarrow$ collective motion of electrons; in a bulk metal, Ohm's law: $V = RI$
- Band structure begins to change when metal particles become small. Discrete energy levels begin to dominate, and Ohm's law is no longer valid.

I-V of a Single Nanoparticle



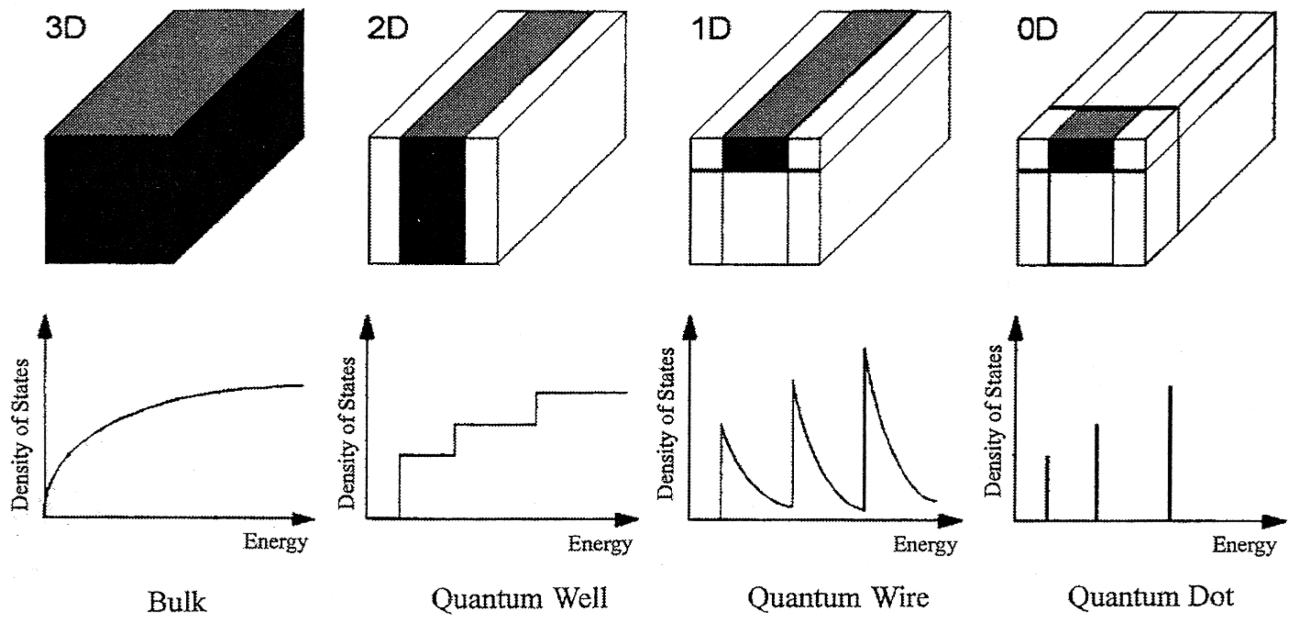


Source: Nanoscale Materials in Chemistry, Wiley, 2001

I-V of a Single Nanoparticle

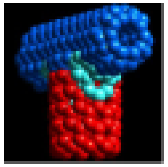
- Consider a single nanoparticle between two electrodes, but cushioned by a capacitance on each side
  - If an electron is transferred to the particle, its coulomb energy $\uparrow$ by $E_c = e^2/2c$
  - Thermal motion of the atoms in the particle can initiate a charge & E_c, leading to further electrons tunneling uncontrollably
  - So, $kT << e^2/2c$
  - Tunneling current $I = V/R_T$
  - Current begins at coulomb voltage $V_c = \pm e/2c$ which is called Coloumb blockade
  - Further electron transfer happens if the coulomb energy of the 'quantum dot' is compensated by an external voltage $V_c = \pm ne/2c$ where n is an integer
  - Repeated tunneling results in a 'staircase' with step height in current e/Rc
  - Possible to charge and discharge a quantum dot in a quantized manner $\Rightarrow$ principle behind some future computers

3D → 2D → 1D → 0D



Source: Nanoscale Materials in Chemistry, Wiley, 2001

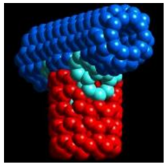
- If a bulk metal is made thinner and thinner, until the electrons can move only in two dimensions (instead of 3), then it is "2D quantum confinement."
- Next level is 'quantum wire
- Ultimately 'quantum dot'



Nanomaterial reinforcement in composites

Ames Research Center

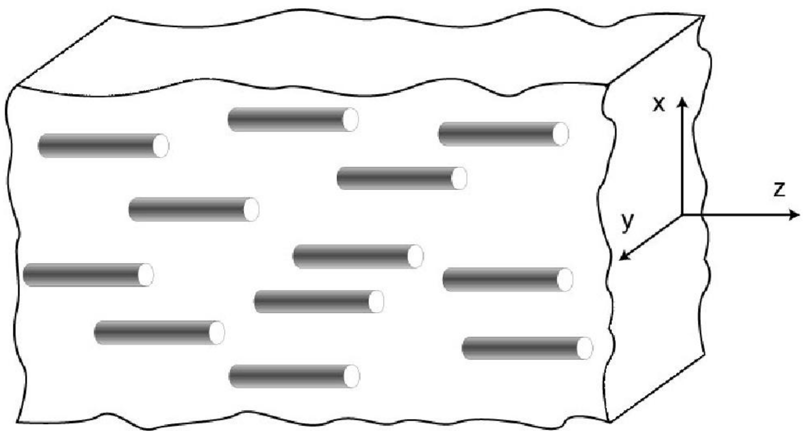
Nano-Reinforced Composites



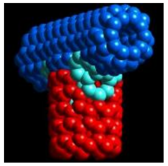
- Processing them into various matrices follow earlier composite developments such as
  - Polymer compounding
  - Producing filled polymers
  - Assembly of laminate composites
  - Polymerizing rigid rod polymers
  -
  -
- Purpose
  - Replace existing materials where properties can be superior
  - Applications where traditionally composites were not a candidate

Benefits of Nanotechnology in Composite Development

- Nanotechnology provides new opportunities for radical changes in composite functionality
- Major benefit is to reach percolation threshold at low volumes (< 1%) when mixing nanoparticles in a host matrix
- Functionalities can be added when we control the orientation of the nanoscale reinforcement.



Multifunctionality in Materials

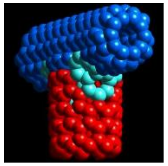


- This always implies “structure +” since in most cases the major function of a structure is to carry load or provide shape. Additional functions can be:
- Actuation → controlling position, shape or load
- Electrical → either insulate or conduct
- Thermal → either insulate or conduct
- Health → monitor, control
- Stealth → managing electromag. or visible signature
- Self-healing → repair localized damage
- Sensing → physical, chemical variables

NRC Report, 2003

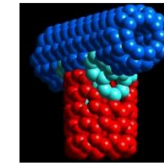
Ames Research Center

Multifunctional Materials with Sensing Capability



- Building in additional functionalities into load-bearing structures is one key example:
  - Sensing function
    - * Strain
    - * Pressure
    - * Temperature
    - * Chemical change
    - * Contaminant presence
- Miniaturized sensors can be embedded in a distributed fashion to add "smartness" or multifunctionality. This approach is 'pre-nano' era.
- Nanotechnology, in contrast, is expected to help in assembling materials with such functional capabilities

Examples of Multifunctional Materials



- Possible, in principle, to design any number of composites with multiple levels of functionality (3, 4, 5…) by using both multifunctional matrices and multifunctional reinforcement additives

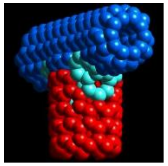
  - Add a capsule into the matrix that contains a nanomaterial sensitive to thermal, mechanical, electrical stress; when this breaks, would indicate the area of damage

  - Another capsule can contain a healant

  - Microcellular structural foam in the matrix may be radar-absorbing, conducting or light-emitting

  - Photovoltaic military uniform also containing Kevlar for protection generate power during sunlight for charging the batteries of various devices in the soldier-gear

NRC Report, 2003



Candidates for Multifunctional Composites

- Carbon nanotubes, nanofibers
- Polymer clay nanocomposites
- Polymer cross-linked aerogels
- Biomimetric hybrids

Expectations:

- ‘Designer’ properties, programmable materials
- High strength, low weight
- Low failure rates
- Reduced life cycle costs