Chair of Condensed Matter Physics
Institute of Theoretical Physics
Faculty of Physics, Universityof Warsaw

Semester Zimowy 2011/2012

Wykład

Modelowanie Nanostruktur

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SZ 2011/2012

Modelowanie Nanostruktur

Program wykładu

***Ab initio* Methods:**

- Density Functional Theory,
- Local Density Approximation (LDA),
- Hartree-Fock method,
- Kohn-Sham Method,
- Concept of Pseudopotential,
- Survey of available numerical codes.

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Modelowanie Nanostruktur

Jacek A. Majewski

- Wykład dla  z podstawową znajomością **Mechaniki Kwantowej**
- **Wykład --- 30 h**
- **Ćwiczenia praktyczne – 45 h**
- Zaliczenie na **ocenę**
- Punkty = pkt. z wykładu (test) + pkt. z ćwiczeń
  Punkty z wykladu = ¼ punktów z ćwiczeń
- **Ocena:** Zalicza > 44% Pkt. , **bdb** > 84%

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Modelowanie Nanostruktur

Program wykładu

Semiempirical Methods for electronic structure calculations:

- Tight-Binding Method
- Pseudopotential Method

Principles of Molecular Dynamics:

- *Ab initio* molecular dynamics (Car-Parrinello method)
- Empirical methods and coarse-graining

Monte Carlo Methods:

- Stochastic and Markov processes, ergodicity,
- Algorithms for Monte Carlo simulations

Continuum methods, (example: Finite Element Method)

Modelowanie Nanostruktur, 2011/2012
Jacek A. Majewski

Wykład 1 – *4 X 2011*

Introduction to
Computational Science,
(Computer Simulations, Computer Modeling),
Computational Materials Science
Modeling of Nanostructures

Why should we bother with it?

Computational Science

- a relatively new discipline
- involves using computers to study *scientific problems*
- complements the areas of theory and experimentation in traditional scientific investigation
- seeks to gain understanding of science principally through the use and analysis of mathematical models on (high performance) computers
- emerged as a powerful and indispensable method of analyzing a variety of problems in research, product and process development, and manufacturing.

→ **Computational Simulations**

Changing the way we do Science ?

Computational Simulations

- *Computer simulations* provide both qualitative and quantitative insights into many phenomena that are too complex to be dealt with by analytical methods or too expensive or dangerous to study by experiments.
- Many experiments and investigations that have traditionally been performed in a laboratory, a wind tunnel, or the field are being augmented or replaced by computer simulations.
- Some studies, such as nuclear repository integrity and global climate change, involve time scales that preclude the use of realistic physical experiments.

Computational Simulations

The availability of

- high performance computers,
- graphic workstations,
- and high speed networks,

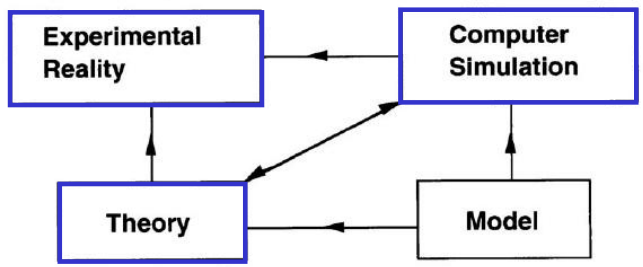
coupled with major advances in algorithms and software, has brought about a revolution in the way scientific and engineering investigations are carried out.

Computational Science vs. Computer Science

- **These two things should not be confused !**
- ***Computational science*** **focuses on a scientific or engineering problem and draws from computer science and mathematics to gain an improved understanding of the problem.**
- ***Computer science*** **focuses on the computer itself.**
- **However,**

  Even though the areas are quite distinct, many of the topics typically considered to be in the domain of computer science are of much value in computational science.

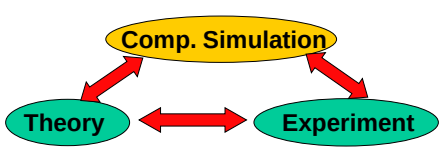
Relationship between modeling, theory and experiment



Dr P. D. Bristowe, University of Cambridge,
Department of Materials Science and Metallurgy

Computational Sciences

- **Computational Physics**
- **Computational Astrophysics and Cosmology**
- **Computational Geophysics**
- **Computational Chemistry**
- **Computational Biology**
- **Computational Engineering**
- **Computational Materials Science**
- **Computational Nanoscience (Modeling of Nanostructures)**

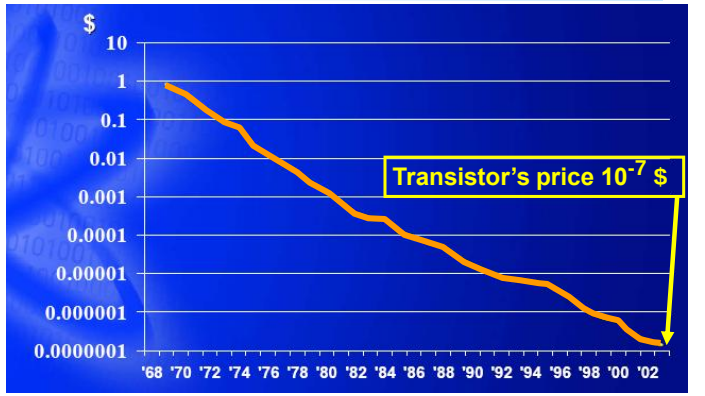


The computer - the hallmark of the information age

- **Computational power has been compounding at an exponential rate for nearly 40 years,**
  - an achievement made possible by advances in silicon processing and fabrication at ever smaller length scales.
- **Breakthroughs in control and fabrication of magnetic media have driven disk capacity to likewise grow exponentially**.

Moore's Law – for processors and memories

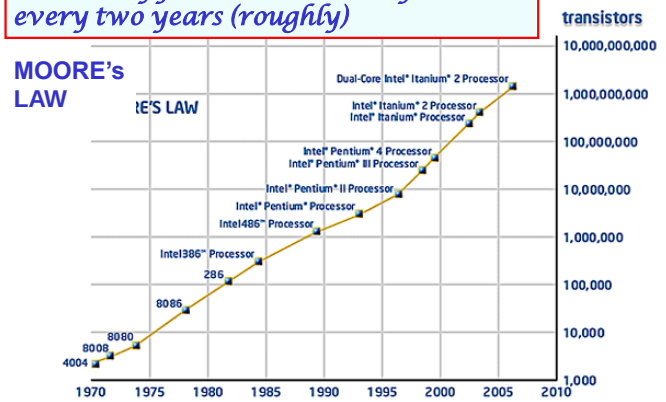
Average price of a transistor



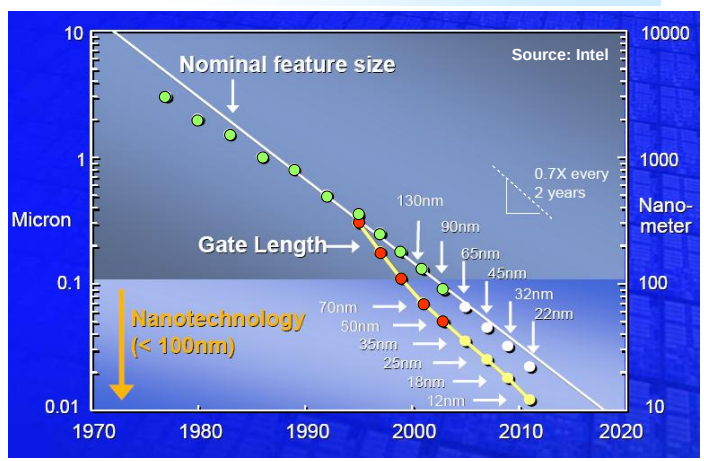
Number of sold transistors in 2002 -- 10^{18}

Exponential progress in integration

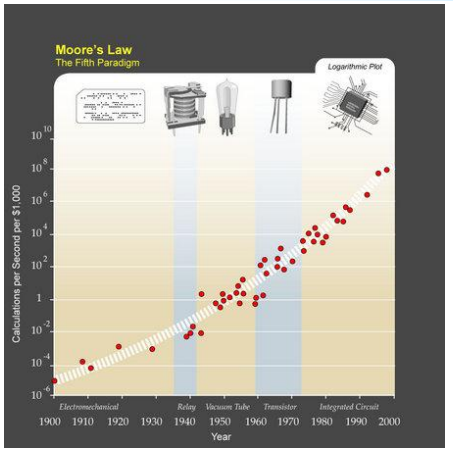
Number of processors on a chip doubles every two years (roughly)



CMOS Technology reaches nano scale



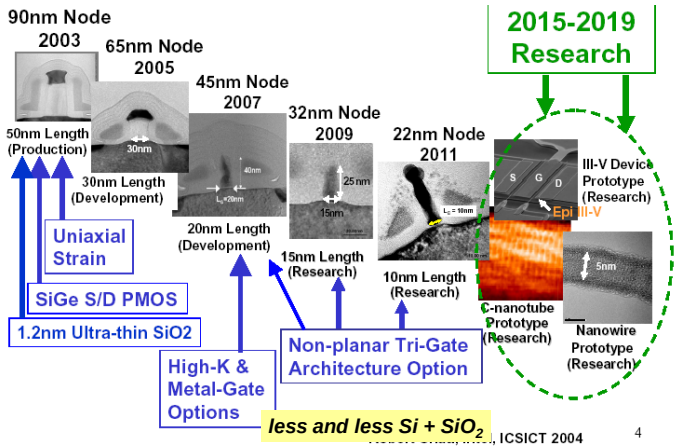
Is it possible to keep exponential character of growth?



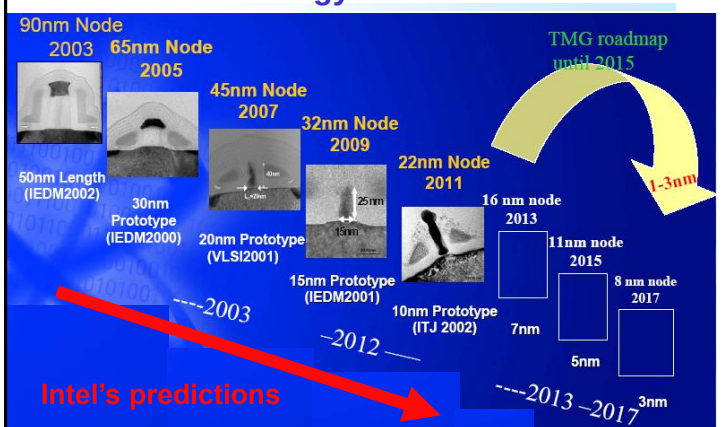
Moore's law is already fifth paradigm concerning computing machines

New technology is going to replace CMOS

Information Technology of the Future

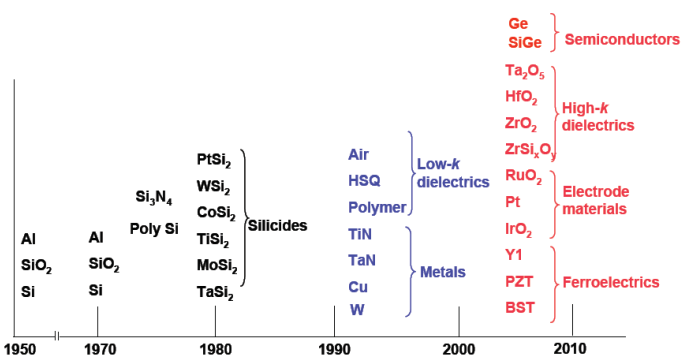


Future development? – 10-15 years CMOS technology will be continued



non-classical CMOS technology

New Materials for Si- Technology



Moore's Law increasingly relies on material innovations

Importance of Materials for Society

The computer is possibly the most visible example of a high tech product that depends critically upon advanced materials

There are many other similar examples that also profoundly affect our lives,

- **new lightweight alloys,**
- **polymers,**
- **composites, etc.**

➡ *Materials Science*

Computational Materials Science - Scales

- Scientists have a handle on the smallest length scale (relevant to materials), which cannot be seen with a microscope, and the largest length scale, which can be seen with the naked eye.
- In between is an intermediate length scale where there are particularly exciting new frontiers.
- The primary scientific challenge is to uncover the elusive connections in the hierarchy of time and length scales and to unravel the complexity of interactions that govern the properties and performance of materials.

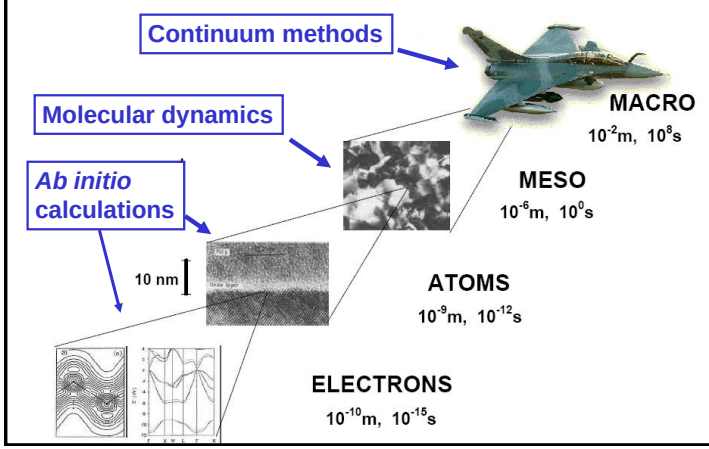
Computational Materials Science

- From the Bronze Age to the silicon-driven Information Age, civilization has defined itself–and advanced itself–by mastering new materials.
- The ability to identify, improve and implement materials -- whether stone, iron, paper, steel or silicon – has profoundly shaped human societies.
- Today, thanks to increasingly powerful computers, the materials science community finds itself on the verge of another revolution.

➡ **extensive computational modeling will complement and sometimes even replace traditional methods of trial-and-error experimentation**.

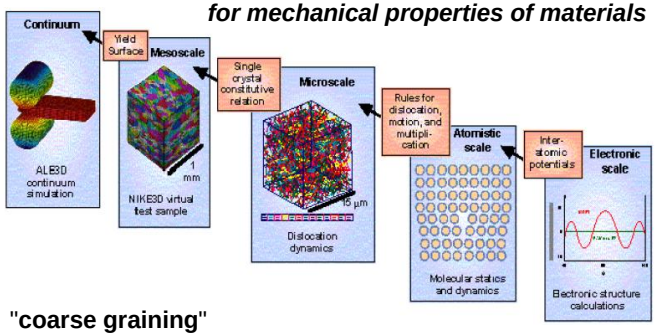
➡ **better understanding and design of new materials**

Connection of atomistic and macroscopic scales



Computational Materials Science – Multi-scale Simulations

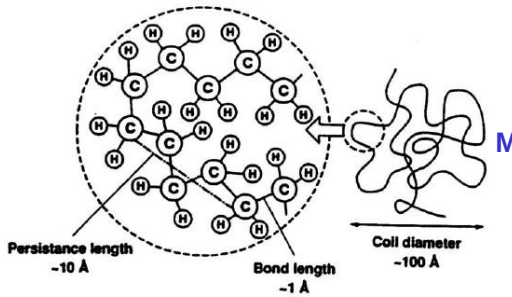
A schematic of the multi-scale challenge for mechanical properties of materials



"**coarse graining**"
the forces among the aggregated pieces can be accurately described by a new model with "renormalized" interactions.

Examples of Models Based on Length Scale (1)

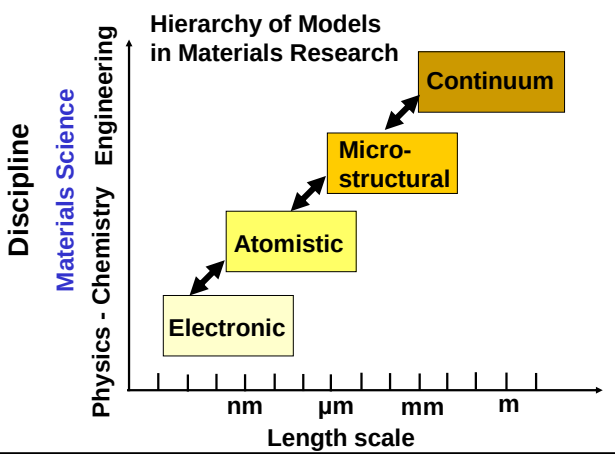
Polymers



Microstructural

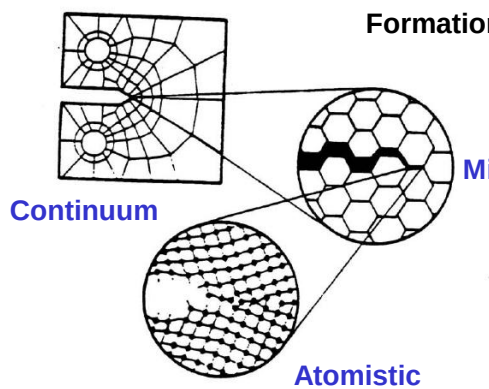
Atomistic **Electronic**

Types of Physical Models Based on Length Scale



Examples of Models Based on Length Scale (2)

Formation of cracks



Microstructural

Continuum

Atomistic

Examples of Computational Simulations

Crack propagation

Cracks happen! (1)

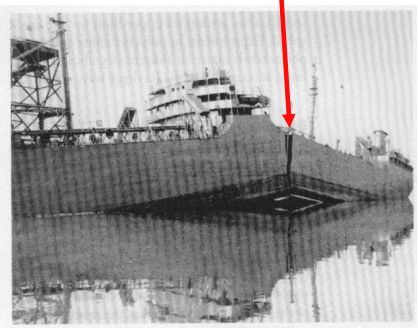


Figure 1. Photograph of the T-2 tanker that failed at its pier: "On January 16, 1943, a T-2 tanker lying quietly at her fitting-out pier at Portland, Oregon, suddenly cracked in a brittle manner…'without warning and with a report that was heard for at least a mile'…."[3] (Photograph courtesy of John Wiley & Sons and the National Academy of Sciences.)

Computational Simulations of Crack Propagation

- **Cracks happen!**

Cracks happen! (2)

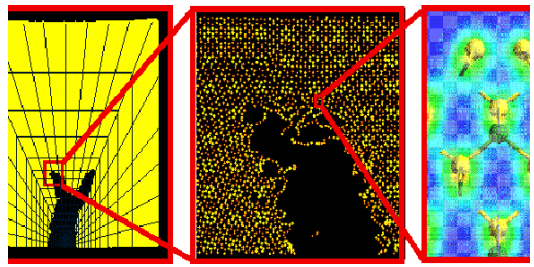
The nucleation and growth of cavities in ductile fracture of metallic materials

Experiment !

Computational Simulations of Crack Propagation

- **Cracks happen!**
- Fracture of materials causes structural damage, loss of productivity, and at times, loss of life.
- However, predicting how and when a material or structure will fail is a difficult task for scientists.
- Why and how things break involve complex fundamental processes and phenomena occurring on a wide range of length and time scales.

Three scales of crack simulations –
Schematic of a multi-scale simulation approach



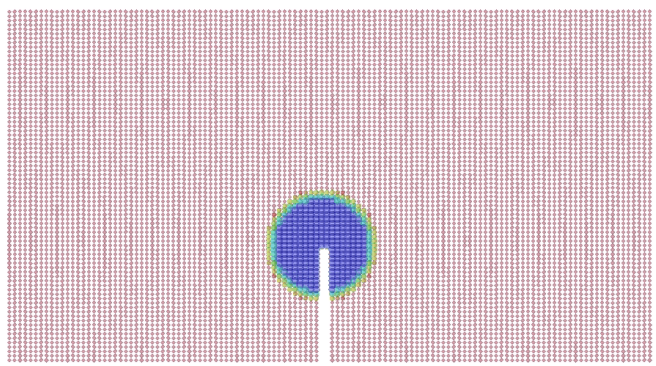
- ***Electronic structure method*** **is combined with** ***molecular dynamics (MD)*** **to describe properly bond breakage and bond formation phenomena.**
- ***The MD*****, in turn, is embedded in the** ***finite-element method*** **to take into account nonlinearities in the system.**

Computational Simulations of Crack Propagation

- Scientists are turning to the largest computers available in order to uncover new clues in solving the mystery of catastrophic materials failure.
- Laboratory testing of materials can reveal fracture strengths and explore the macroscopic reasons for fracture.
- Material scientists know that, ultimately, ***fracture involves breaking bonds between the atoms that make up the solid***.

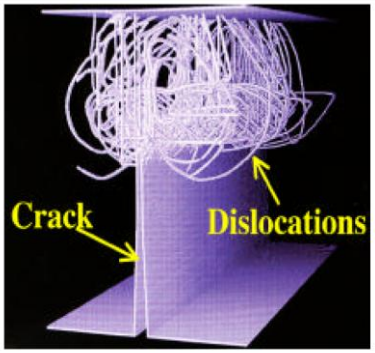
⟹ **Computers are ideal for studying these local, atomistic processes.**

Computational Simulations of Crack Propagation



Computational Simulations of Crack Propagation

The simulation illustrates some of the complex events that occur as a crack moves in a ductile metal.



Atomistic model of crack propagation in ductile metal

- At first, the crack moves very rapidly and local bonds break in a "brittle" manner,
- but at some point the crack-tip begins to emit dislocations and stops propagating.

⇒ ***blunted crack***

Examples of Computational Simulations

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

Computational Simulations of Crack Propagation

- ***A blunted crack*** can cause intense local deformation, but it does not cause failure.
- ***Cracks that can emit dislocations usually stop before complete structural failure occurs.***
- However, when the material is unable to emit dislocations, crack propagation does not terminate, which eventually leads to failure and irreversible damage of the material.
- The fundamental phenomena that determine whether a material is able to emit the beneficial dislocations are yet to be elucidated.

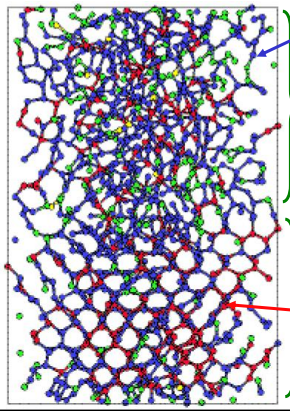
⇒ **design of new materials and composites**

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

- Well beyond its value for jewelry, **diamond is invaluable as the hardest known substance**.
- Fine diamond particles are the ultimate abrasive, and wear resistant diamond coatings are used on tools from saw blades to surgical instruments.
- But who would consider melting diamond?
- Materials scientists and engineers who are searching for cheaper and more robust processing routes to the synthesis of diamond coatings could use the thermodynamic phase diagram of carbon as a guide.
- **The conditions that it takes to melt diamond are too extreme for careful laboratory experimentation**.

Melting A Diamond Crystal with Tight Binding Molecular Dynamics

A snapshot of 2000 carbon atoms (T>6000 K)



Blue atoms indicate three-fold (graphitic) bonded atoms

two-fold and five-fold coordinated atoms

Red atoms indicate four-fold bonded (diamond-like) atoms

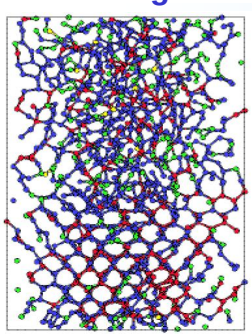
Melting A Diamond Crystal with TB Molecular Dynamics - Significance

- Experiments that are difficult, expensive, or impossible in the laboratory, can be accurately simulated on modern computers.
- By including the essential quantum nature of the electrons and their chemical bonds, the tight binding calculations form a natural ***bridge*** leading from first principles electronic structure calculations ***to the mesoscopic regime***.

➡ Extension of the quantum mechanical treatment to even larger numbers of atoms in order to investigate more complex nanoscale phenomena involving extended defects.

- **This would illuminate the fundamental relationship between *microstructure* and important *macroscopic materials properties*.**

Melting A Diamond Crystal with Tight Binding Molecular Dynamics



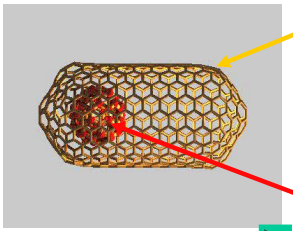
- The large number of three-fold atoms is an indication that the liquid phase is less dense than the four-fold diamond phase.
- By changing temperature and/or pressure, the interface between the solid and liquid will move (e.g., the solid fraction increases below the melting point).

Such simulations permit the accurate determination of the melting temperature of diamond as a function of pressure.

Examples of Computational Simulations

- **Future nano-electronics**
- **Chemical reactions**
- **Computational biology**

Simulation of a nanotube-based memory element

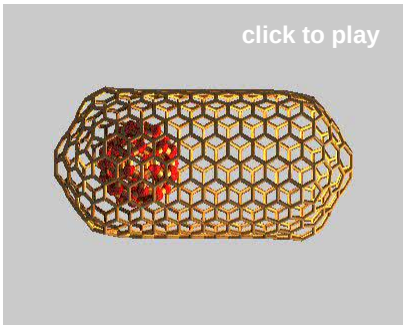


The outer capsule - short segment of (10,10) carbon nanotube with diameter 1.4 nm terminated at both ends by perfect fullerene caps.

The capsule is large enough to hold a C_{60} buckyball molecule inside.

- The buckyball carries a net charge if it contains an alkali atom in the hollow cage.
- **The C_{60} molecule can be shifted from one end to the other by applying an *electric field* between the ends of the capsule**

Simulation of a nanotube-based memory element

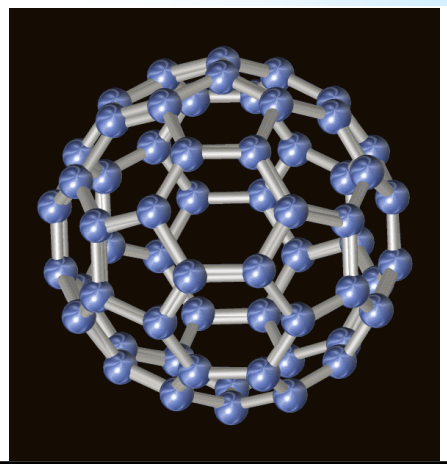


The **two energy minima** of this system, with the buckyball bonded to either end of the capsule, can be associated with **bit 0** and **bit 1**.

The simulation has been performed by Young-Kyun Kwon

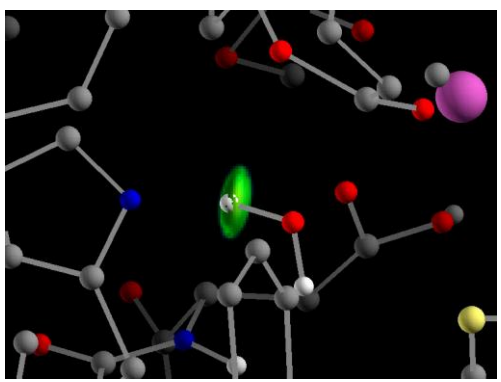
This structure has been patented as a non-volatile memory element and awarded U.S. Patent No. 6,473,351

Fullerene (buckyball)

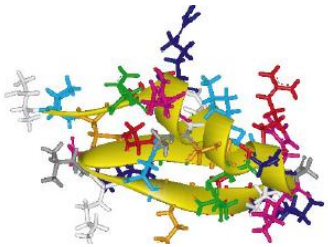


Ab initio MD Simulations of Chemical Reaction

Dissociation of water molecule

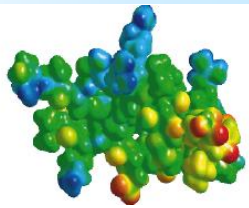


DFT as a new tool for computational biology



Structure of the 1PNH protein, a scorpion toxin (PO_5-NH_2)

- It consists of 31 amino acid Residues (ca. 500 atoms)
- Different colors are used to represent different amino acids



Electrostatic potential for electrons

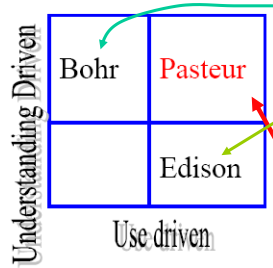
- Zero value – green
- Repulsive regions – red and yellow
- Attractive regions - blue

Role of the protein charge state on the geometry – change of the charge state of the protein does not destabilize the local energy minima

Computational Materials Science: A Scientific Revolution about to Materialize

- Due to the complexity of materials systems, progress has necessarily proceeded either within the Bohr quadrant or Edison's quadrant

Pasteur's Quadrant



experiment and theory done on model systems

research and development by trial and error

Realistic simulation is the vehicle for moving materials research firmly into Pasteur's quadrant.

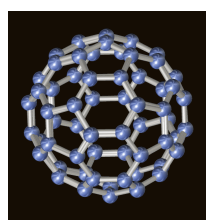
Computational Materials Science: A Scientific Revolution about to Materialize

- The materials science community is on the verge of a paradigm shift in the way it does science with the promise of building a sturdy bridge across the "valley of death" between basic science and technological impact.
- A useful construct for thinking about this potential paradigm is "**Pasteur's Quadrant**."

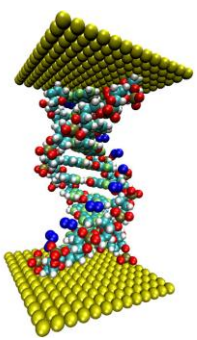
D. E. Stokes, *"Pasteur's Quadrant, Basic Science and Technological Innovation,,*
The Brookings Institution, Washington D.C., 1997

Fundamental problem in materials science

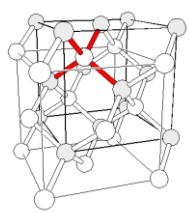
A fundamental problem in materials science is the prediction of condensed matter's electronic structure



C_{60} - molecule



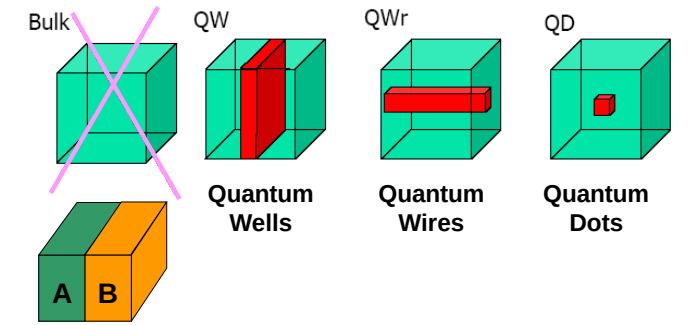
DNA - molecule



Crystal - diamond

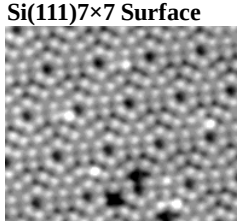
Modeling Nanostructures

Nanotechnology – Low Dimensional Structures

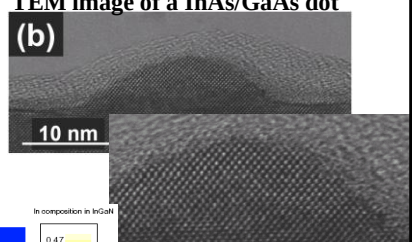


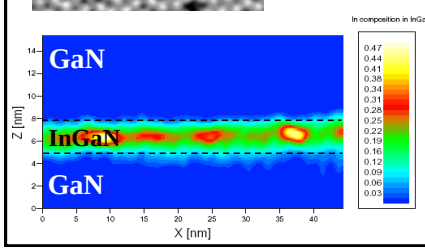
Examples of Nanostructures

Si(111)7×7 Surface



TEM image of a InAs/GaAs dot





HRTEM image: segregation of Indium in GaN/InGaN Quantum Well

What about realistic nanostructures ?

Inorganics

3D (bulks) : **1-10** atoms in the unit cell

2D (quantum wells): **10-100** atoms in the unit cell

1D (quantum wires): **1 K-10 K** atoms in the unit cell

0D (quantum dots): **100K-1000 K** atoms in the unit cell

Organics

Nanotubes, DNA: **100-1000** atoms (or more)

Atomistic methods for modeling of nanostructures

- *Ab initio* methods (up to few hundred atoms)
- **Semiempirical methods** (up to 1M atoms)
  - Empirical Pseudopotential
  - **Tight-Binding Methods**

Materials Science: Examples of Schrödinger Equation?

- **Materials are composed of nuclei** $\{Z_\alpha, M_\alpha, \vec{R}_\alpha\}$ **and electrons** $\{\vec{r}_i\}$
  → **the interactions are known**

$$H = -\sum_\alpha \frac{\hbar^2 \nabla_\alpha^2}{2M_\alpha} - \sum_i \frac{\hbar^2 \nabla_i^2}{2m} + \frac{1}{2}\sum_{\alpha,\beta} \frac{Z_\alpha Z_\beta e^2}{|\vec{R}_\alpha - \vec{R}_\beta|} - \sum_{i,\alpha} \frac{Z_\alpha e^2}{|\vec{R}_\alpha - \vec{r}_i|} + \frac{1}{2}\sum_{i,j} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}$$

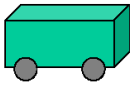
Kinetic energy of nuclei; Kinetic energy of electrons; Nucleus-Nucleus interaction; Electron-Nucleus interaction; Electron-Electron interaction

$$H\Psi = E\Psi$$

***Ab-initio* (first principles) Method – ONLY Atomic Numbers $\{Z_i\}$ as input parameters**

Materials Science: Why *ab-initio* approach is needed?

- **A model as simple as possible**

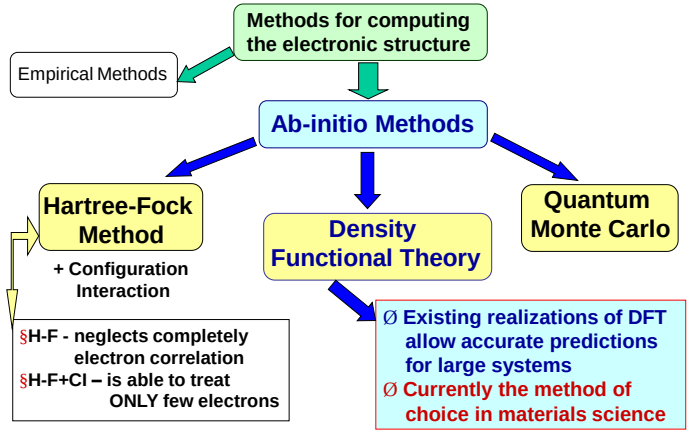


- **A model non-empirical and realistic**

- **Explanation and extrapolation of experimental results**
- **Physical insight**
- **Qualitative physics**

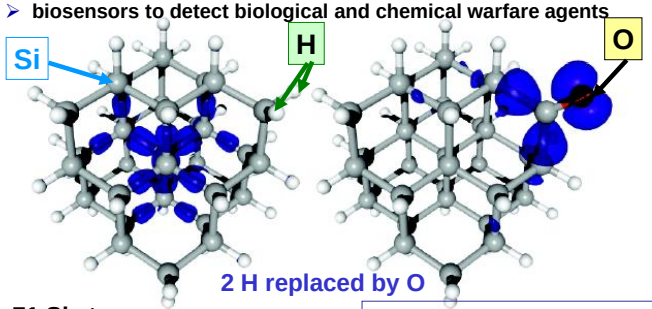
- **Reliable predictions of matter's properties**
- **Design of new materials**
- **Unexpected phenomena and unusual conditions (e.g., extreme pressures)**

Spectrum of Electronic Hamiltonian: What *ab initio* methods do we have?



DFT for silicon nanostructures

Silicon nanoparticles (clusters, dots)
- optoelectronic materials on silicon basis
- biosensors to detect biological and chemical warfare agents



- 71 Si atoms 'passivated' by hydrogens
- Electrons are in the center of the dot

Dramatic change of the optical properties (wavelength) of the silicon nanostructure

G. Gali & F. Gygi, Lawrence Livermore National Laboratory

Tight-Binding methods

Computational Materials Science – The Era of Applied Quantum Mechanics

The properties of new and artificially structured materials can be predicted and explained
- *entirely by computations,*
- *using atomic numbers as the only input .*

Thank you !

Tight-Binding Formalism

$$\varphi_n(\vec{r}) = \sum_{\alpha,i} c_n^{\alpha i}\, \chi_{\alpha i}(\vec{r})$$

$\{\chi_{\alpha i}\}$ orthogonal set of functions → NOT ATOMIC ORBITALS !

index of orbital; index of atom

$$\varepsilon_n = \langle \varphi_n | H | \varphi_n \rangle = \sum_{i\alpha}\sum_{j\beta} (c_n^{\alpha i})^* c_n^{\beta j} \langle i\alpha | H | j\beta \rangle$$

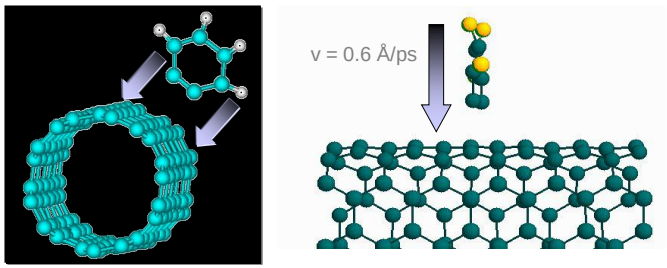
Tight –binding Hamiltonian

$$H = \sum_{\alpha i} \varepsilon_{i\alpha} |i\alpha\rangle\langle i\alpha| + \sum_{\alpha i,\beta j} t_{i\alpha,j\beta} |i\alpha\rangle\langle j\beta|$$

on-site; hoping TB-parameters

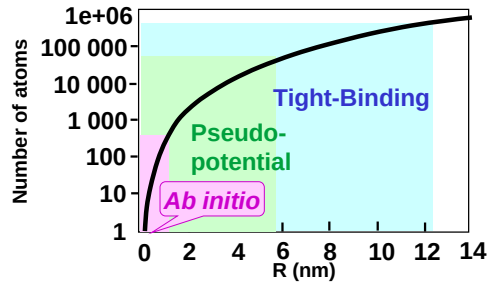
Green's Function + Molecular dynamics
Carbon Nanotubes

- **Molecular Dynamics** simulations of a reactive collision of a biased nanotube (V=100mV) and benzene
- **Current** flowing in the nanotube calculated at each MD step



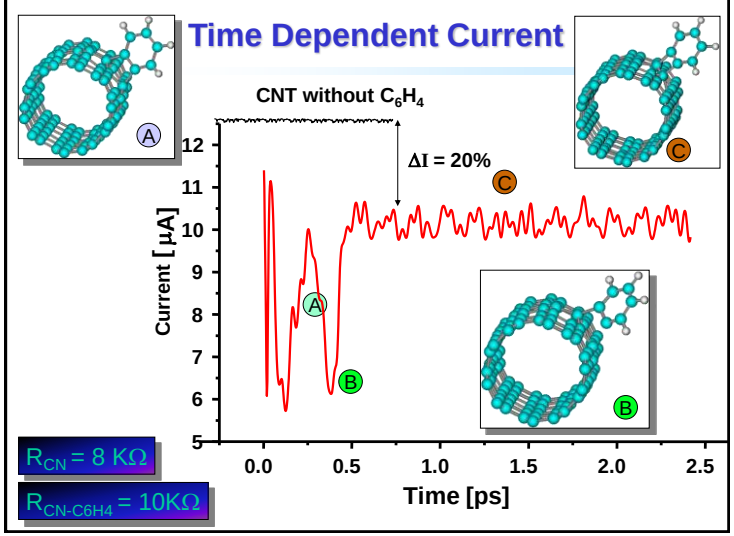
Conclusions

- **Microscopic approaches can be applied to calculate properties of realistic nanostructures**



Number of atoms in a spherical Si nanocrystal as a function of its radius R.
Current limits of the main techniques for calculating electronic structure.
Nanostructures commonly studied experimentally lie in the size range 2-15 nm.

Time Dependent Current



Continuum theory- Envelope Function Theory

Electron in an external field

$$\left[\frac{\hat{p}^2}{2m} + V(\vec{r}) + U(\vec{r})\right]\psi(\vec{r}) = \varepsilon\psi(\vec{r})$$

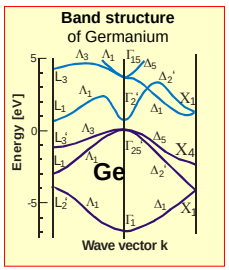
Periodic potential of crystal

Non-periodic external potential

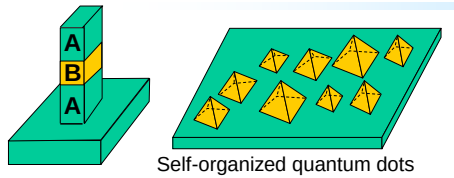
- Strongly varying on atomic scale
- Slowly varying on atomic scale

Band Structure

$U(\vec{r}) = 0 \Rightarrow \varepsilon_n(\vec{k}) \Rightarrow$



Electron States in Quantum Dots



Self-organized quantum dots

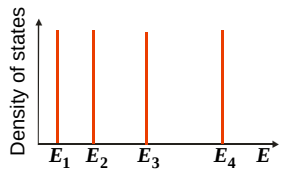
Electrons confined in all directions

$U(x,y,z)$

$$-\frac{\hbar^2}{2m^*}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)F_n(x,y,z)+U(x,y,z)F_n(x,y,z)=E_nF_n(x,y,z)$$

Density of states for zero dimensional (0D) electrons (artificial atoms)

$$G^{(0D)}(E)=\sum_{\nu}\delta(E-E_{\nu})$$



Envelope Function Theory – Effective Mass Equation

J. M. Luttinger & W. Kohn, Phys. Rev. B **97**, 869 (1955).

$$[\varepsilon(-i\vec{\nabla}) + U(\vec{r}) - \varepsilon]F_n(\vec{r}) = 0$$ (EME)

EME does not couple different bands

$$\psi(\vec{r}) = F_n(\vec{r})u_{n0}(\vec{r})$$

"True" wavefunction — Envelope Function — Periodic Bloch Function

- Special case of constant (or zero) external potential

$U(\vec{r}) = 0 \Rightarrow F_n(\vec{r}) = \exp(i\vec{k}\cdot\vec{r}) \Rightarrow \psi(\vec{r})$ **Bloch function**

- $U(z) \Rightarrow F_n(\vec{r}) = \exp[i(k_x x + k_y y)]F_n(z)$

Calculation of the strain tensor

Elastic energy $E = \frac{1}{2}\int C_{ijkl}(\vec{x})\varepsilon_{ij}(\vec{x})\varepsilon_{kl}(\vec{x})d\vec{x}$

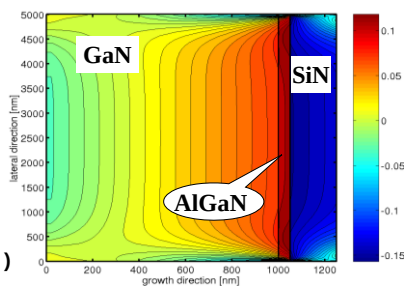
Minimization of elastic energy gives the strain distribution $\varepsilon_{kl}(\vec{x})$

It corresponds to $\frac{\partial\sigma_{ij}}{\partial x_i} = 0$

$\sigma_{ij} = C_{ijkl}\varepsilon_{kl}$

Hook's Law

Strain Map



(for GaN/AlGaN HEMT)

3D nano-device simulator - nextnano^3

Simulator for 3D semiconductor nano-structures:

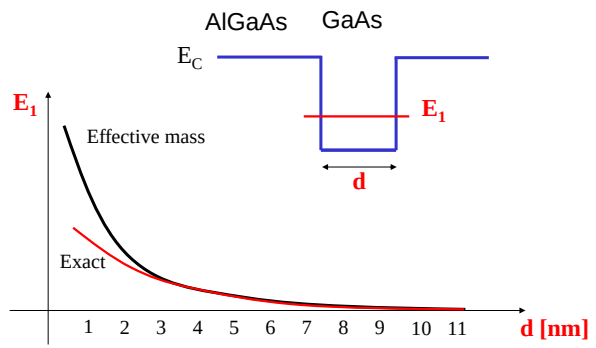
- Si/Ge and III-V materials
- Flexible structures & geometries
- Fully quantum mechanical
- Equilibrium & nonequilibrium

Calculation of electronic structure :

- 8-band kp-Schrödinger+Poisson equation
- Global strain minimization
- Piezo- and pyroelectric charges
- Exciton energies, optical matrix elements,...

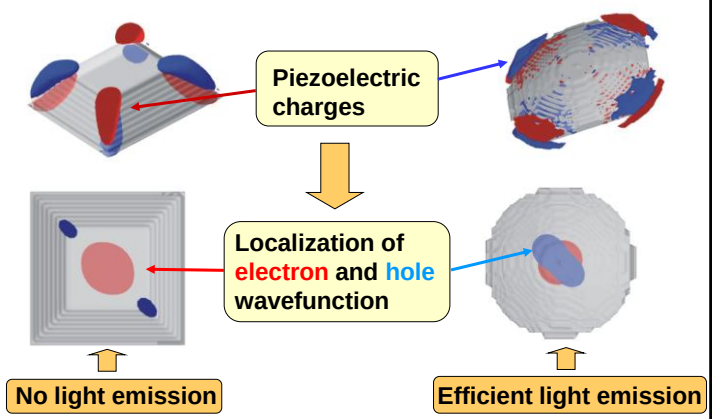
Calculation of current only close to equilibrium with new approach

How good is effective mass aprox. ?



- **Atomistic details sometimes matter !**

Dot shape and piezoelectric charges



Software for nanostructures modeling

http://www.facebook.com/pages/List-of-software-for-nanostructures-modeling/144056828940389

Modeling of nanostructures at classical and quantum levels.

facebook

Ascalaph Designer
Atomistix ToolKit & Virtual NanoLab
CST STUDIO SUITE(TM)
CoNTub
Nanohub allows simulating geometry, electronic properties and electrical transport phenomena in various nanostructures
Nanorex
NEMO 3-D enables multi-million atom electronic structure simulations in empirical tight binding. It is open source. An educational version is on nanoHUB as well as Quantum Dot Lab
.....

Usage of NanoHub (http://nanohub.org)

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- Z. H. Barber (ed), ***Introduction to Materials Modelling***, (Maney, 2005)
- J. M. Haile**, *Molecular Dynamics Simulation*** (Wiley 1992)

Thank you!