Hierarchy of device simulation approaches

- Quantum Approaches
- Boltzmann Equation
- Monte Carlo particle Approaches
- Moments of Boltzmann Equation (Hydrodynamics Approach)
- Drift-Diffusion Approaches
- Compact Models
Trends in traditional device research

- Large scale integrated circuits are dominated by MOS devices
- Commercial devices are already fabricated with gate length shorter than 100 nm.
- Laboratory devices are built with sub 10 nm gate length.

“bulk” MOSFET
Trends in traditional device research

• The performance of “bulk” MOSFETs degrades with scaling.
• Doping fluctuations make it difficult to build a large number of devices with more or less identical behavior. New oxide materials are considered to overcome limitations of very thin SiO$_2$.
• New structures are being investigated to pursue the nanoscale limits of silicon technology. These are still “MOSFETs”

Examples: Double-gate MOSFET, FinFET

![Diagram of a double-gate MOSFET and a FinFET]

- $n^+$
- $p^-$
- $D$
- $S$
- $G$
- $G_f$
- $G_b$
- $t_{Si}$
- $t_{oxf}$
- $t_{oxb}$
- fin (height = 10 nm)
The Quest for a replacement of the MOSFET

- Molecular devices – Example of a single molecule structure (diode) between contacts. A chain of molecules could also be used.
Typical response of a molecular device
Molecular Devices

- Molecular cellular automata (C. Lent et al., 2003)
- This structure would reduce the “energy dissipation” problem.

(a) “1”

(b) “0”
Inorganic Alternatives

- Carbon nanotubes – obtained by rolling a graphene sheet
Examples of nanotubes

• (a) “Armchair” and (b) “zigzag” carbon nanotubes
Simplified Band Structure of Zigzag CNT

$E \; \; [\; \; eV\; \; ]$

$k_z \; [\; \; 2\pi / T \; \; ]$
Comparison of transport properties

Electric Field [ kV/cm ]

Drift velocity [ $10^7$ cm/s ]

(10,0) CNT

GaAs

Si
CNT Field Effect Transistors

- Most practical approaches have tried to create a transistor by using a gate terminal (field effect) to control the current in a CNT conducting channel.

From: [www.infineon.com](http://www.infineon.com)

Even a metallic CNT transistor has been conceived (Rotkin and Hess, APL, 2004)
Possible Hybrid Solution

- CNTs “implanted” in the channel of a MOSFET

From: www.research.ibm.com
Potential for interconnects

- From: www.infineon.com
- Catalyst mediated CVD growth at moderate temperatures (600°C)
Comments on Simulation Approaches 1

- Molecular chains and carbon nanotube conducting channels may be simulated at the quantum level as quasi-1-D conductors with a very similar Green’s function methodology, using a different Hamiltonian for the system.
- Density functional theory in the GGA approximation has been widely adopted to represent the Hamiltonian of organic molecular system. Very popular is the B3PW91 model, obtained from merging the Beck-3 (exchange) Perdew-Wang 91 (correlation) models.
- Gaussian-98 (www.gaussian.com) is the most commonly used computational chemistry code for DFT calculations.
- The molecule Hamiltonian is not enough, one also needs the Hamiltonian for the contacts (molecular alligator clip) consisting, typically of sulphur transition atom connected to gold (thiol group). DFT has also been used for this purpose, but an LCAO approximation may be sufficient (Crystal-98 code has been used in the literature).
Comments on Simulation Approaches 2

- Other variations found in the literature adopt a scheme called density-functional-tight-binding (DFTB). This is based on a second order expansion of the Kohn-Sham total energy with respect to charge density fluctuations.

- The 0th order approach would be equivalent to the standard non-self-consistent tight-binding (TB) scheme, where the Hamiltonian eigenstates are expanded into an orthogonalized basis of atomic-like orbitals.

- The DFTB is based on a two-center approximation for the Hamiltonian matrix elements, explicitly calculated with a non-orthogonal basis of atomic orbitals.

- DFTB is particularly useful for the analysis of structural and energetic properties of molecular systems, because of the introduction of self-consistency.
Comments on Simulation Approaches 3

STEPS in simulating a “device-like” structure

• Formulate the Hamiltonian of the molecular system $H$
• Formulate the contact self-energies $\Sigma_1$ and $\Sigma_2$ to create an “open system”
• Generate the Green function of the complete system

$$ G = \left(E S - H - \Sigma_1 - \Sigma_2 \right)^{-1} $$

• Obtain the transmission coefficient from the Green function, $T(E)$

$$ T(E) = \text{Tr} \left[ A_1 M A_2 M^\dagger \right] \quad \text{where} \quad M = \tau_1 G \tau_2^\dagger $$

• Relate the transmission coefficient to conduction properties, e.g. the resistance using the Landauer formula for 1-D conductor

$$ R = \frac{h}{2e^2} \frac{1}{T(E_f)} $$
• “Long” carbon nanotube structures may be studied with semi-classical methods, assuming a 1-D conduction.

• Scattering rates by phonons can be derived for the subband structure. Intra- and inter-subband scattering mechanisms should be considered.

• Because of the quasi-1-D nature of the system scattering may be forward or backward. With a careful selection of diameter, one may find a situation where scattering is virtually suppressed in theory ⇒ ballistic transport.

• Continuum (e.g., drift-diffusion) and particle (Monte Carlo) simulation approaches could be used, at different levels of approximation.

• The nature of the metal-CNT contact is certainly important. It could correspond to a Schottky barrier, involving tunneling mechanisms for injection.
Carbon nanotube bandstructure is sensitive to electric field.
We consider here a simple TB approach to include the field effect.

Tight Binding Method

On-site energy \( \varepsilon \)
Hopping integral \( t \)

\( \varepsilon_A, \varepsilon_B, \varepsilon_C, \varepsilon_D, \varepsilon_{AB}, \varepsilon_{AD}, \varepsilon_{BC}, \varepsilon_{BD}, \varepsilon_{CD} \)

Nearest neighbor (n.n.) approximation

- On-site energy

- Every carbon atom has 3 nearest neighbors, with hopping integral
Assign matrix elements $H^0_{i,j}$

Example (5,0) CNT

Initialize $H^0$

$H^0 = 0$
Assign matrix elements $H_{i,j}^0$

Example (5,0) CNT

Assign n.n. interactions within the unit cell

$H^0(i,j) = \gamma$

June 11, 2004
Summer School 2004
Umberto Ravaiolli
Assign matrix elements $H^0_{i,j}$

Example (5,0) CNT

n.n. interaction between unit cells
Assign matrix elements $H_{i,j}^0$

Example (5,0) CNT

Shift the interaction back into the unit cell

$H^0(i, j) = \gamma \exp(ik\Delta z)$
Stark Effect: a perpendicular electric field

\[ V = V_0 \sin \theta \]

Solve perturbed Hamiltonian for new eigen-states and eigen-energies
Stark Effect of a (10,10) Armchair CNT

$E = 0 - 0.3 \text{ V/Å}$,  
$\Delta E = 0.03 \text{ V/Å}$ (10 frames)
Stark Effect of a (17,0) Zigzag CNT

\[ E = 0 - 0.3 \text{ V/Å}, \]
\[ \Delta E = 0.03 \text{ V/Å} \text{ (10 frames)} \]
Stark Effect of an (18,0) Zigzag CNT

E=0-0.3 V/Å ,
ΔE=0.03V/Å (10 frames)
It's all in this applet at www.amanogawa.com
Wet / dry environments

- "Biological" computers (e.g., brain) use electric conduction in electrolytes. Typical solvent is water, but other solutions are possible.
- Detection problems often involve sensor devices in wet environments (e.g., Lab-on-a-chip and Bio-MEMS).
- The Holy-Grail is single molecule detection.
- The biological work-horses for electrical signaling in wet environment are the ionic channels. In-depth discussion on ionic channel by T. van der Straaten on June 17 presentation.
- Bio-inspired structures may involve nanopores or carbon nanotubes in artificial membranes. Functionalization is the process that decorates such channels to modify their electrical behavior and achieve function.
- Biomimetics is the term use for artificial structures that aim at duplicating the function of a biological system.
Ionic channels

[Diagram showing ions (+ and -) moving through a membrane with water on either side]
Carbon nanotube channels

J. Mashl et al.,
Nano Letters, 2003
Ionic channels

• Some examples

Gramicidin A

ompF porin
## Times scales

<table>
<thead>
<tr>
<th>Time scale</th>
<th>Phenomena</th>
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<tr>
<td>femtoseconds</td>
<td>Bond stretching, breaking and bending</td>
</tr>
<tr>
<td>picoseconds</td>
<td>Hydrogen bond lifetimes</td>
</tr>
<tr>
<td>nanoseconds</td>
<td>Diffusion times for small ions to move by nanometers</td>
</tr>
<tr>
<td>microseconds</td>
<td>Statistically meaningful ion transport to define system state</td>
</tr>
<tr>
<td>milliseconds and more</td>
<td>Nanoscale molecular assemblies undergo significant conformational changes</td>
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## Space scales

<table>
<thead>
<tr>
<th>Space scale</th>
<th>Physical features and applications</th>
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<tr>
<td>Atomic and subatomic</td>
<td>Electronic structure of molecules</td>
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<td>Molecular</td>
<td>Conformational searches. Molecular simulation and molecular electrostatics</td>
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<td>Brownian dynamics</td>
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<tr>
<td>Continuum</td>
<td>Diffusion, migration, fluid flow</td>
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</tbody>
</table>
Simulation issues

- A complete simulation would involve molecular models with atomic resolution and a quantum description. EXTREMELY EXPENSIVE

- Much work is conducted with essentially classical molecular dynamics to determine motion of molecules and electrolyte. Quantum mechanics is used to determine inputs like the charge distribution on the molecular structure (many approximations are usually involved, as well as various descriptions of atomic components of the molecules).

- Molecular dynamics cannot yet resolve “biological times”. In practices one may be able to simulate tens of nanosecond for typical structures.
Simulation issues

- A snapshot of molecular dynamics calculation with GROMACS code (courtesy S.-W. Chiu and E. Jakobsson, UIUC).
Simulation issues

- A reduced order model is necessary to probe biological times.

- Typical approaches:
  - Brownian dynamics (BD) / Transport Monte Carlo (TMC)
    - Water, protein and lipid are treated as a continuum media with a certain dielectric permittivity
    - Partial charges are distributed on protein
    - Ions movement is treated in detail. Coupling with water is accomplished from the knowledge of diffusivity translated into random forces (BD) or scattering rates (TMC)

  - Continuum flow: Drift-Diffusion or Poisson-Nernst-Planck (PNP) model
    - Ions are simulated as continuum flow, similarly to the treatment of electrons and holes in a semiconductor device.
    - The size of the ion is not included in the original formulation of these models. Potential correction terms could be added to include finite ion size.
Abstraction of continuum model

• The translation of molecular structure into a continuum with a specific dielectric permittivity is a crucial step.
• Molecular structure is not rigid. How can we capture the molecular movement in a continuum model?
• What are the actual boundaries between protein, lipid and water?
• Dielectric permittivity may be vastly different between the various regions ⇒ image force at dielectric boundaries can be significant.
• Screening of charge is very different in a continuum or in a particle (granular) picture. Electrostatic field solution may yield different results.
Simple nanopore in a membrane

Image force near the dielectric boundary creates a barrier for ion permeation

\[
\begin{align*}
\varepsilon & \quad 1 \\
\varepsilon & \quad 1
\end{align*}
\]

water \( \varepsilon = 80 \varepsilon_0 \)
Ionic channel in a membrane

Image force evaluation is even more complicated. The protein has a strongly non-uniform charge distribution. Also, what should the permittivity of water be in the narrow channel?

water $\varepsilon = 80 \varepsilon_0$
Useful Web resources

- [www.nanohub.org](http://www.nanohub.org) is the portal of the Network for Computational Nanotechnology. Contains a number of tools for nanoelectronics, including molecular structures. We will use it in the second week of the School.

- [www.ks.uiuc.edu](http://www.ks.uiuc.edu) site of Theoretical Biophysics group at UIUC (Prof. Schulten) has the NAMD molecular dynamics code and other molecular tools. We plan to use the VMD tool on Tuesday next week.

- [www.gromacs.org](http://www.gromacs.org) GROMACS molecular dynamics code.

- [thallium.med.cornell.edu/RouxLab/](http://thallium.med.cornell.edu/RouxLab/) Prof. Roux’s web site has a number of ion channel tools available.