People on board: international multiscale modeling network

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Study nanodevices and peek into the black box

- Many devices are **black boxes**, in the sense that **input-output** relations (response functions) are known, but we know much less about their internal structures.
- Their inner mechanisms are usually studied with continuum theories (for example, PNP for semiconductor devices)
- Dimensions of the devices, however, continuously shrink (nanodevices)
- The **molecular behavior** of the **core unit** of the device (that can be very different from bulk behavior) determines **device behavior**
- We need to study the **core unit** on the molecular level with **modeling** and **computation**
Core units and the devices „around” them have different length/time scales

- Different length and time scales
- Different techniques to deal with them
- What is the relation of the different levels?
In our studies, the core units are porous materials

Examples: ion channels in biological membranes, synthetic nanopores, silicate membranes (zeolite, silicalite, kaolinite)

Phenomena of interest: selectivity, permeation, rectification

Models: from all-atom to coarse-grained (reduced)

Motivation: technology, biology
Nanopore as a device – a rectifying diode

- Pore etched into plastic foil
- Dimensions: $\mu$m length, nm radius
- **Input**: voltage
- **Output**: current
- Engineering point of view: voltage-current relation

Black box response function

But what is in the black box?

- **Input**: voltage in the nanopore, $V_N$ (V)
- **Output**: current, $I$ (nA)

Dezső Boda (U. Pannonia, iASK, Hungary)
Nanopore fabrication

- Motivation: semiconductor p-n junctions

- PDMS or PET nanopores

(a) Ion-track-etching technique

(b) Schematic of nanopore fabrication process:

1. Irradiation
2. Chemical etching
Resolution of the microscopic model – multiscaling

- Detailed model vs. reduced model to handle subsystems with different scales
- Advantages/disadvantages (too many details vs. too much approximation)
- Reduced models for large-scale device properties, all-atom models for molecular details
- The challenge is to link the various modeling levels

**Hierarchy of models and methods**

- Explicit water (MD) → implicit water (BD, LEMC, PNP)
- Direct simulation of transport (BD) → transport equation (NP)
- Particle simulation (LEMC) → continuum method (PNP)

### Decreasing resolution (and computation time)

<table>
<thead>
<tr>
<th>WEEKS</th>
<th>DAYS</th>
<th>DAYS</th>
<th>HOURS</th>
<th>SECONDS</th>
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<tbody>
<tr>
<td>All-atom</td>
<td>Reduced (e.g., implicit solvent)</td>
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**MD**
- Molecular Dynamics
- Direct simulation of transport
- Newton equations

**BD**
- Brownian Dynamics
- Direct simulation of transport
- Langevin equations

**DMC**
- Dynamic Monte Carlo
- Mimic trajectories

**LEMC**
- Local Equilibrium Monte Carlo
- \( c_i(r) \leftrightarrow \mu_i(r) \)

**NP+LEMC**
- Nernst-Planck transport equation
- \(-kT j_i(r) = D_i(r) c_i(r) \nabla \mu_i(r)\)

**PB**
- Poisson-Boltzmann
- \( c_i(r) \leftrightarrow \mu_i(r) \)

**PNP**
- Multiscale modeling of nanodevices
- Dezső Boda (U. Pannonia, iASK, Hungary)
- Veszprém, 2017.11.02.
Electrodiffusion: the Nernst-Planck equation

\[
j^\alpha(r) = -\frac{1}{kT} D^\alpha(r) c^\alpha(r) \nabla \mu^\alpha(r)
\]

- **Flux**: output of the calculation – \( j^\alpha(r) \)
- **Concentration**: availability of the transported particles – \( c^\alpha(r) \)
- **Diffusion coefficient**: mobility of the transported particles – \( D^\alpha(r) \)
- **Driving force**: difference/gradient of the electrochemical potential – \( \mu^\alpha(r) \)

What is the relation of \( c^\alpha(r) \) and \( \mu^\alpha(r) \) in the transport (non-equilibrium) region?

Non-equilibrium statistical mechanics is needed. Not well-established.

General solution: divide the system into volume elements and assume **local equilibrium** (LE) in them.

Use the procedures of equilibrium statistical mechanics in the volume elements.

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Statistical mechanical methods that can be used

The electrochemical potential:

$$\mu^\alpha(r) = \mu_0^\alpha + kT \ln c^\alpha(r) + \mu_{EX}^\alpha + z^\alpha e\Phi(r)$$

- **Poisson-Boltzmann**: used for the ideal solution ($\mu_{EX}^\alpha(r) = 0$) – NP+PB (traditionally called Poisson-Nernst-Planck (PNP) theory)

- **Density Functional Theory** (Tarazona, Gillespie) – NP+DFT (1D)

- **Simulation (our suggestion)**: perform GCMC simulation using different electrochemical potentials in the volume elements (each element is an open system in the GC ensemble) – **Local Equilibrium Monte Carlo** (LEMC)

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Solution domain (pore + access regions) is divided into volume elements ($V_i$).

**Input:** $\mu^\alpha(r_i)$, **Output:** $c^\alpha(r_i)$

**Acceptance probability** for inserting ($\chi = 1$) or deleting ($\chi = -1$) an ion in a volume element (below).

$N_i^\alpha$ is the number of ions in $V_i$ **before** insertion/deletion.

The energy contains the interactions with **everything** in the whole simulation cell including the applied field ($r \in V_i$).

$$p_{i,\chi}^\alpha(r) = \frac{N_i^\alpha! V_i^\chi}{(N_i^\alpha + \chi)!} \exp \left( -\frac{\Delta U(r) - \chi \mu_i^\alpha}{kT} \right)$$
Reduced models reproduce experimental data for device behavior properly.

Why do reduced models work?

Reduced models reproduce experimental data for device behavior properly. Why is that?

How can reduced models work while they ignore seemingly important molecular details (water, for example)?

Our answer is that they work, because they get those properties right that are important for device behavior.

In the case of nanopores/channels, it is the axial behavior of concentration profiles.

When we build a reduced model by ignoring certain degrees of freedom, we can ignore the „unimportant” ones and we must include the „important” ones in the model.

How do you distinguish „important” and „unimportant” details is the art of multiscaling. Sometimes, it is obvious. Sometimes, it is not.
Thanks for your attention!