# Multiscale modeling of rectifying bipolar nanopore: explicit-water versus implicit-water simulations

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## Introduction

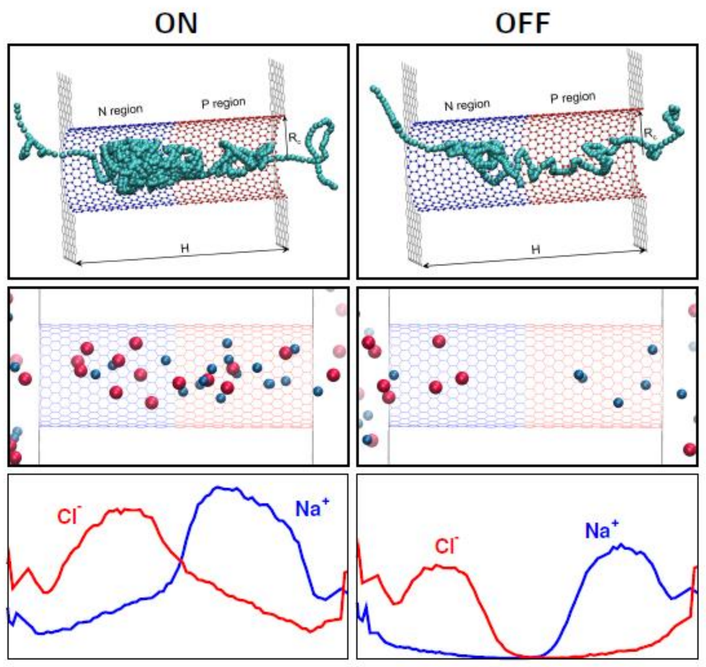
We present results for a nanodevice on two disctinct modeling levels. In an *all-atom model*, we use explicit water to simulate ion transport directly with the Molecular Dynamics (MD) technique. In *a reduced model*, we use an implicit water model and apply the Local Equilibrium Monte Carlo method together with the Nernst-Planck transport equation (NP+LEMC). The device under study is a rectifying bipolar nanopore.

We are interested in the question why the reduced model (the implicit-water model) can reproduce device behavior (rectification) despite the fact that important molecular details (explicit water, for example) are ignored and/or approximated. Our results show that reduced models work if they contain those degrees of freedom that are relevant for device function. The crucial step in multiscaling is to find connection between the two modeling levels. In this case, the diffusion coefficient in the pore is fitted to MD results.

## Models

| | All-atom model | Reduced model |
|---|---|---|
| Method | Molecular Dynamics | NP+LEMC |
| Ions | LJ+point charge | HS+point charge |
| Water | SPC | Dielectric continuum |
| Pore | Carbon nanotube | Hard wall+point charges |
| Membrane | Carbon nanosheets | Hard wall |
| Computing time | Days | Hours |

## Illustration of the geometry and the rectification mechanism




## NP+LEMC Method

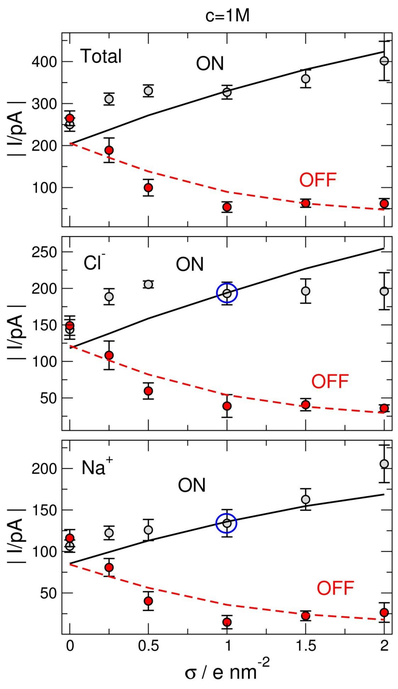
The ionic flux computed with the Nernst- Planck (NP) equation of electrodiffusion:

$$-kT\boldsymbol{j_i}(\boldsymbol{r}) = D_i(\boldsymbol{r})c_i(\boldsymbol{r})\nabla\mu_i(\boldsymbol{r})$$

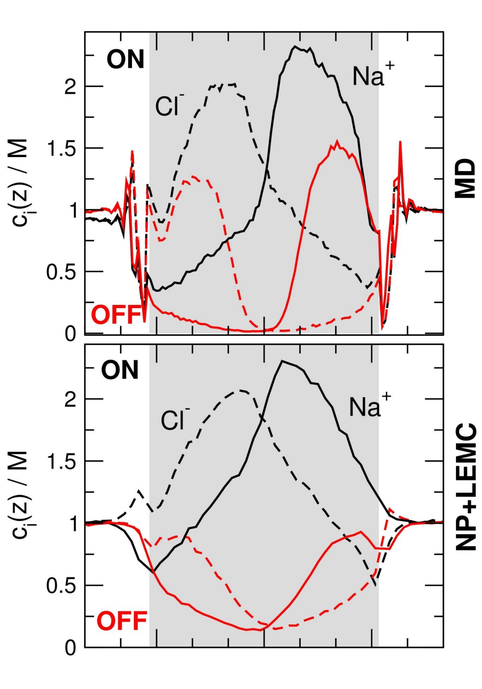
- $\boldsymbol{j}_i(\boldsymbol{r})$ particle flux density of ionic species $i$,
- $k$ Boltzmann's constant
- $T$ temperature
- $c_i(\boldsymbol{r})$ concentration profile
- $\mu_i(\boldsymbol{r})$ electrochemical potential profile

- The relation between $c_i(\boldsymbol{r})$ and $\mu_i(\boldsymbol{r})$ is established with Local Equilibrium Monte Carlo simulation (LEMC)
- LEMC is a grand canonical MC simulation devised for a non-equilibrium situation.
- The computation domain of the NP system is divided into volume elements with different $\mu_i$ values
- The whole system is solved in an iterative way until conservation of mass is satisfied.

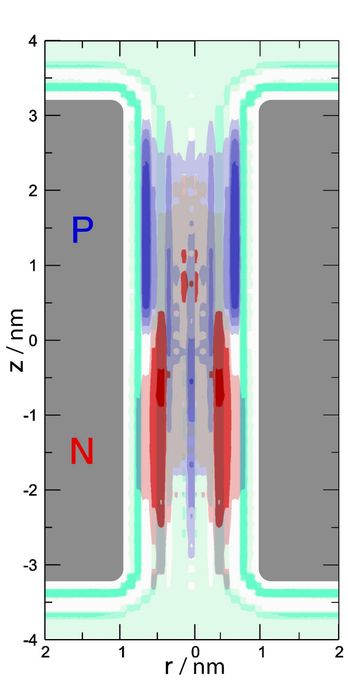
## Results



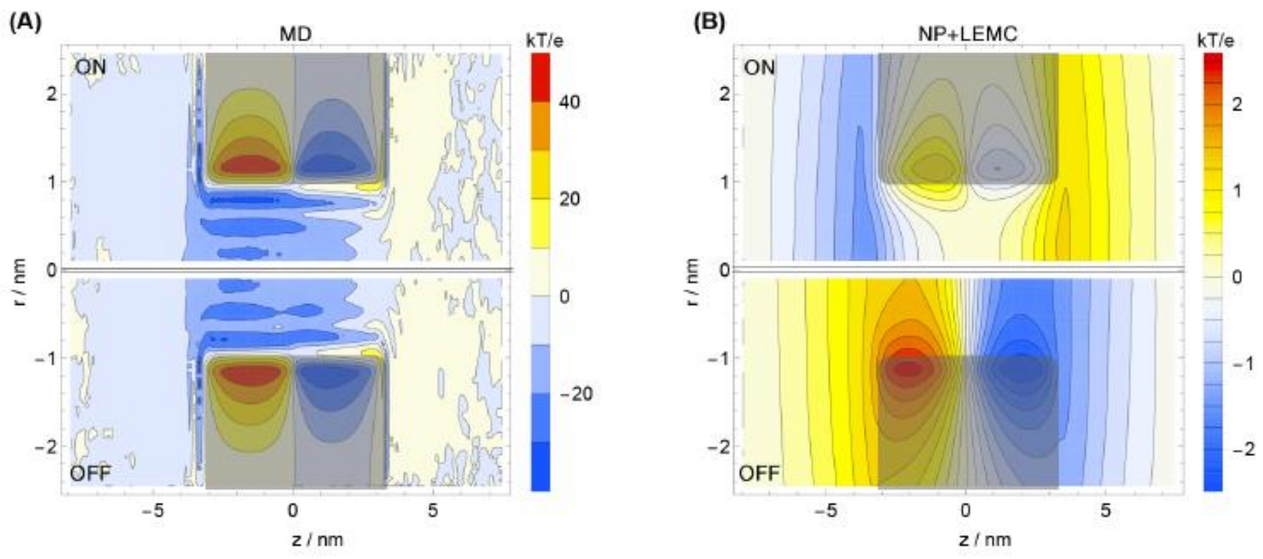

Currents as functions of surface charge density for $c$=1M for the ON (200mV) and OFF (-200mV) sign of the voltage. Lines: NP+LEMC, symbols: MD. Blue circles: where pore diffusion coefficients were fitted.




$Na^+$ (solid) and $Cl^-$ (dashed) axial concentration profiles as obtained from MD and NP+LEMC in the ON (black) and OFF (red) signs of the voltage for $c$=1M and $\sigma$=1$e$/nm$^2$.




$Na^+$ (blue), $Cl^-$ (red), and water (turuoise) contour plots as obtained from MD in the ON state. NP+LEMC provides structureless ionic profiles and no water profile.




Mean electrical potential profiles as obtained from MD and NP+LEMC simulations. The profiles do not include the applied potential. The MD profiles include the contributions of fixed charges (on the pore wall), ions, and water. The MC profiles include only the effect of fixed charges and ions divided by ε.

## Summary

We found definite differences between the results of the explicit and implicit-water models with respect to

- how they describe the radial dependence of the particle profiles,
- whether the double layers on the two sides of the membrane are formed or not,
- how the screening of ionic and pore charges by water is done.

Still, the $z$-dependence of the ionic concentration profiles is similar in the two models. That is the important molecular detail from the point of view of device function.

Reduced models show what device level physics is necessary/sufficient to predict device characteristics and to design new devices.

## References

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