

Modeling and simulating complex ionic systems in the presence of dielectric inhomogeneities

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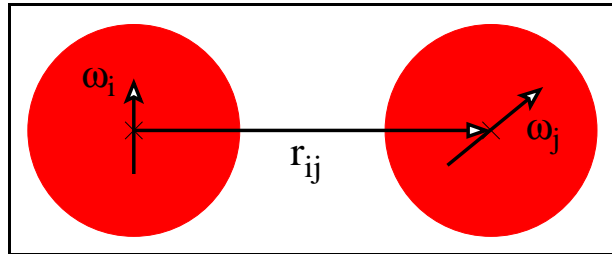
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Molecular models - two particle system



$$u(\mathbf{r}_{12}, \boldsymbol{\omega}_1, \boldsymbol{\omega}_2)$$

Intermolecular pair potential

- depends on the mutual position (\mathbf{r}_{ij})
- and the mutual orientations ($\boldsymbol{\omega}_i, \boldsymbol{\omega}_j$) of the molecules
- It can be calculated from quantum mechanics or we can use **model potentials**.

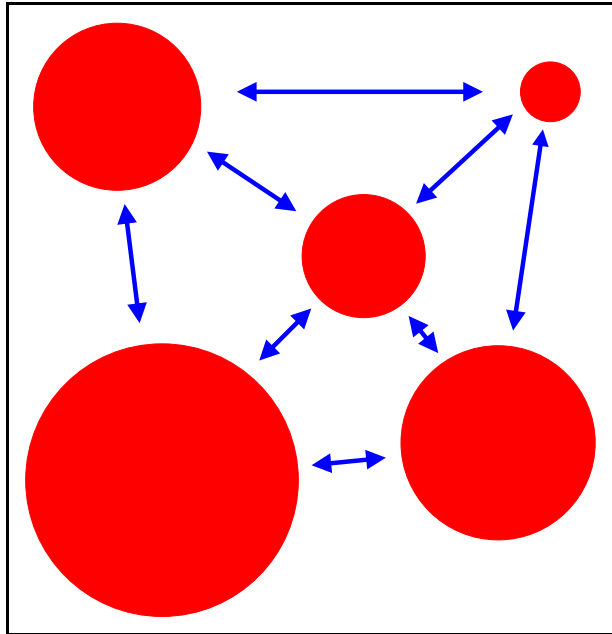
It is usual to **divide** the model potential into

- repulsive core (hard sphere, exponential, or $1/r^{12}$ repulsion)
- attractive dispersion force ($1/r^6$ or exponential Yukawa attraction)
- electrostatic forces (Coulomb, dipole, quadrupole, etc.)

Example: SPC/E water

- a Lennard-Jones potential $4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$ on the oxygen
- and partial charges on the atoms
- 6 parameters: 2 LJ parameters, 2 partial charges, distance and angle of hydrogens

Molecular models - many particle systems



Intermolecular potentials

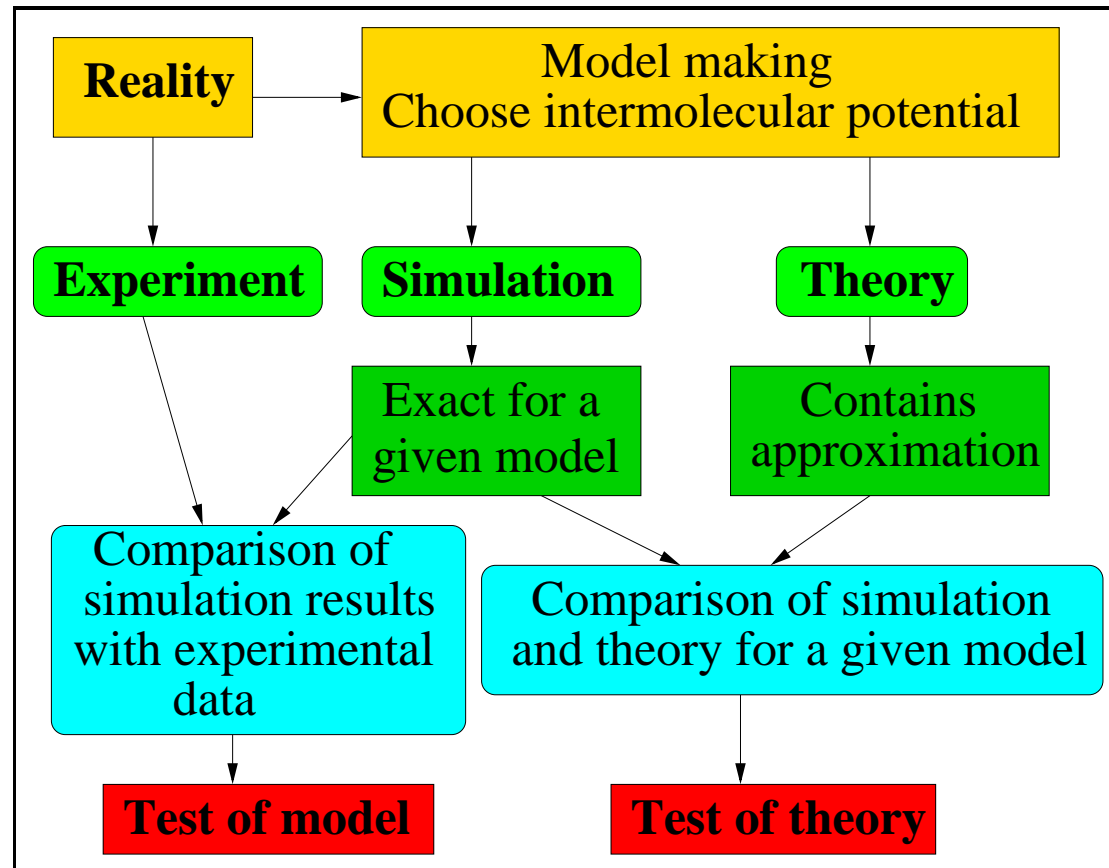
acting between particles

- defines the system on the *microscopic level*
- determines the **energy** for a given configuration of the particles

- The energy is not equal to the sum of the pair potentials: $U \neq \sum_{i < j} u_{ij}$
- The difference is due to **many body forces**
- the vicinity of a third particle changes the pair potential
- **Solution:** using *effective* pair potentials
- fit the parameters of the potential to experimental results
- For instance: fit vapour-liquid equilibrium curves
- **How can we relate the microscopic pair potential to measured physical quantities?**

STATISTICAL MECHANICS

The relation of the microscopic and the macroscopic level



Computer simulations serve as a bridge between real systems and their models

- **What is simulation?**
Theory? Experiment?
- **Answer:** a statistical mechanical tool that gives *exact results*
- **apart from** *statistical uncertainty* and *system size* problems.
- A **theory** has to be verified by comparison to simulation.
- A **model** has to be verified by comparing the simulation results to macroscopic experimental data.

Statistical mechanics

- The **thermodynamic state** has to be specified. For example: **canonical ensemble** - number of particles (N), volume (V), and temperature (T) are fixed.
- The macroscopic quantities of the system are known if the partition function is known: $Q = \sum_i \exp(-U_i/kT)$, where we sum over the possible states of the system and U_i is the energy in state i . In the classical theory the sum becomes an integral over phase space (position and velocity).
- For example: Helmholtz free energy: $F = -kT \ln Q$, etc.
- **Ensemble average** of physical quantity B is $\langle B \rangle = \frac{1}{Q} \sum_i B_i \exp(-U_i/kT)$, where B_i is the value of B in state i - calculated by **Monte Carlo** (MC) simulation
- **Time average** of the physical quantity B is $\bar{B} = \frac{1}{\tau} \int B(t) dt$ - calculated by **molecular dynamics** (MD) simulation
- **Postulate**: the two averages are equal - $\langle B \rangle = \bar{B}$.

Molecular dynamics simulation

- We move the particles according to the equations of motions of Newton - a deterministic approach.
- The force acting on each particles is known if the intermolecular potentials are specified.
- Choosing a small Δt time interval, we can calculate the velocities and positions of the particles at time $t + \Delta t$ if we know the velocities and positions at time t .
- In the simulation, we calculate and store the various physical quantities and we calculate the *time average* at the end.
- Appropriate to simulate **non-equilibrium** systems and **dynamical properties** (e. g. diffusion).
- **Problems:** native ensemble is NVE (microcanonical).
- Application to other ensembles: sort of mixing of MD and MC.
- Problems with thermostating.

Monte Carlo simulations

A simplified picture

- We randomly sample the phase space - hence the name
- **First idea:** generate random possible states uniformly and estimate

$$Q = \sum_i \exp(-U_i/kT)$$

- The ensemble average of B would be $\langle B \rangle = \sum_i B_i p_i$.
- where $p_i = \frac{1}{Q} \exp(-U_i/kT)$ is the probability of state i .
- **Problem:** the number of possible states is huge.
- We sample states that are far from equilibrium: U_i is large; $\exp(-U_i/kT)$ is small.
- Their contribution to Q is small - they are *not important*.
- **Solution:** *importance sampling* - we sample states that are important

Monte Carlo simulations

Importance sampling

- Let us generate states with p_i probability (Boltzmann sampling).
- We have to bias in the ensemble average with the Boltzmann factor:

$$\langle B \rangle = \frac{\sum_i B_i \exp(-U_i/kT)/p_i}{\sum_i \exp(-U_i/kT)/p_i} = \frac{\sum_i B_i}{M}$$

where M is the number of generated states.

- This is a simple mean average.
- Realization of this sampling: **Metropolis sampling**
N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, E. Teller, *Chem. Phys.* 1953, **21**, 1087. (simulation of hard disks - Los Alamos)
- There are a lot of other possibilities.

Monte Carlo simulations

Metropolis sampling

- Probability of transition $i \rightarrow i + 1$ is

$$p_{i \rightarrow i+1} = p_{i+1}/p_i = \exp[-(U_{i+1} - U_i)/kT] = \exp(-\Delta U/kT)$$

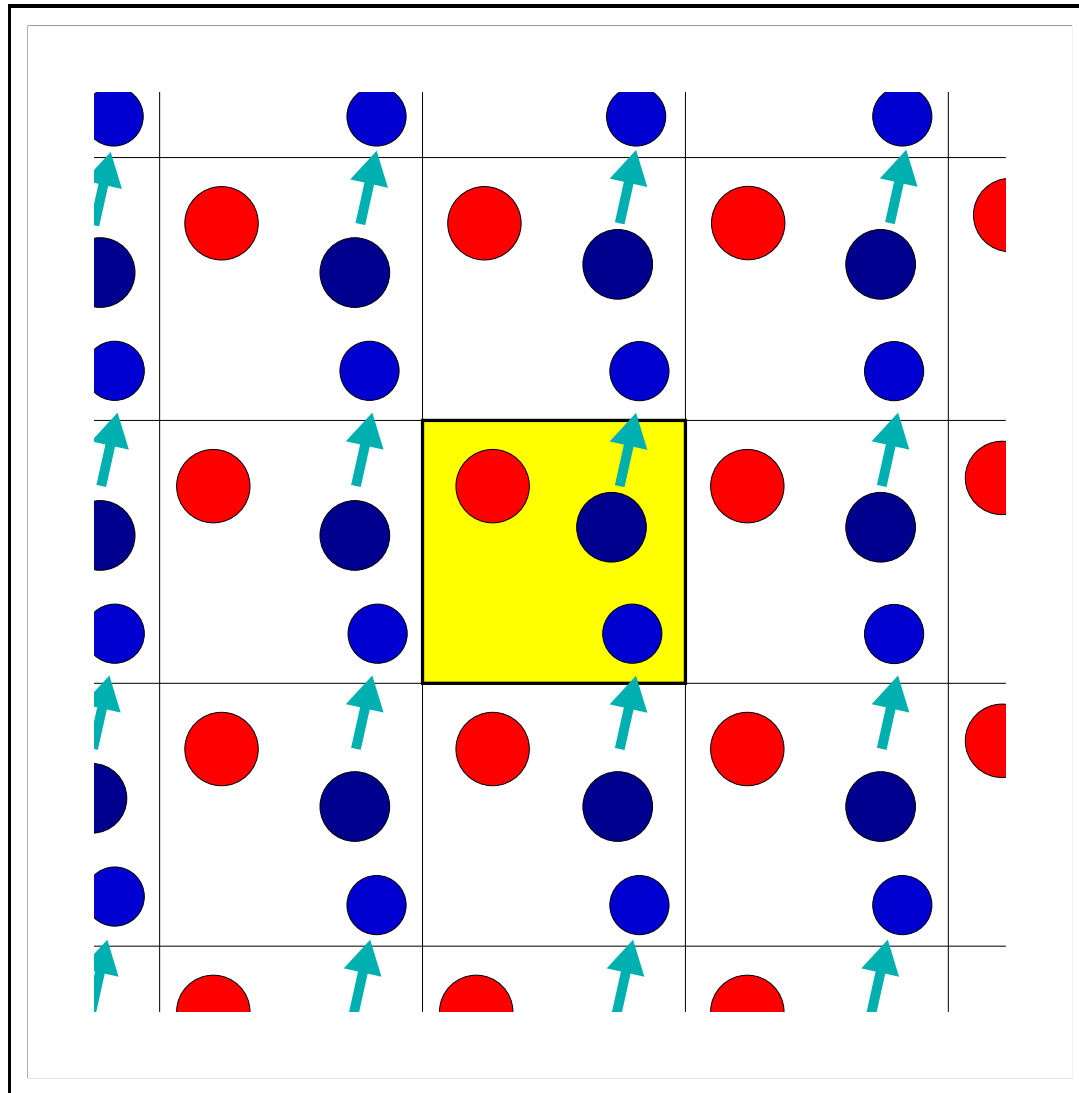
- State $i + 1$ is accepted by relating to the previous state i - a Markov chain.
- The new state is accepted with the probability $\min[1, \exp(-\Delta U/kT)]$.
- The MC step is always accepted if $\Delta U < 0$.
- When $\Delta U > 0$, it is accepted with probability $\exp(-\Delta U/kT)$
- This is a Boltzmann sampling.

Monte Carlo simulations

Other ensembles

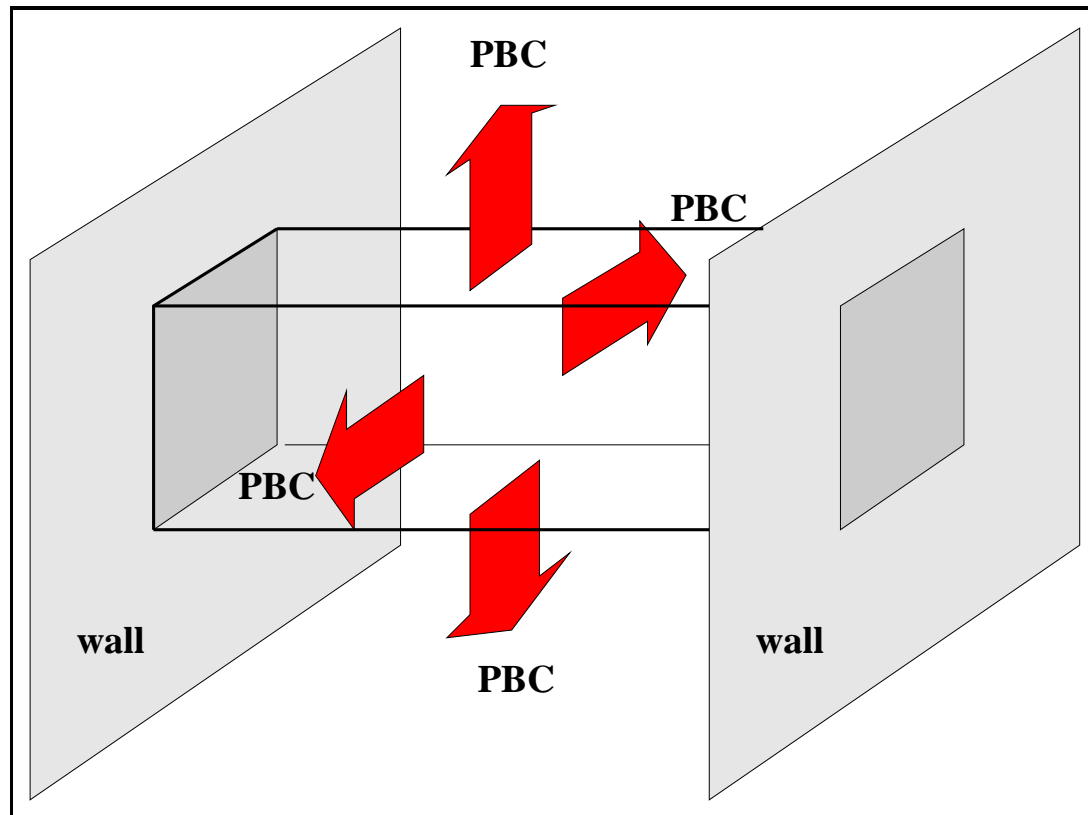
- NpT : **fixed pressure** - volume change
- μVT **grand canonical**: fixed chemical potential - particle insertion/deletion
- **Gibbs ensemble** - two simulation boxes with particle and volume exchange - simulation of phase equilibria
- **Biased moves**: to improve the efficiency of sampling and accelerate simulations
- **Example**: particle exchange between a small volume subsystem (ion channel) and a large volume subsystem (bath).
- Normally, such moves are rare and sampling of occupancy of the channel is inefficient.

Periodic boundary condition



- **imitation** of macroscopic (infinite) sample
- the Universe is filled with the **periodic images** of the central simulation cell
- if a particle moved out of the central simulation cell, its periodic image is coming back in from the other side
- **surface effects** are eliminated
- **other problems:** enforced periodicity, system size dependence prevails

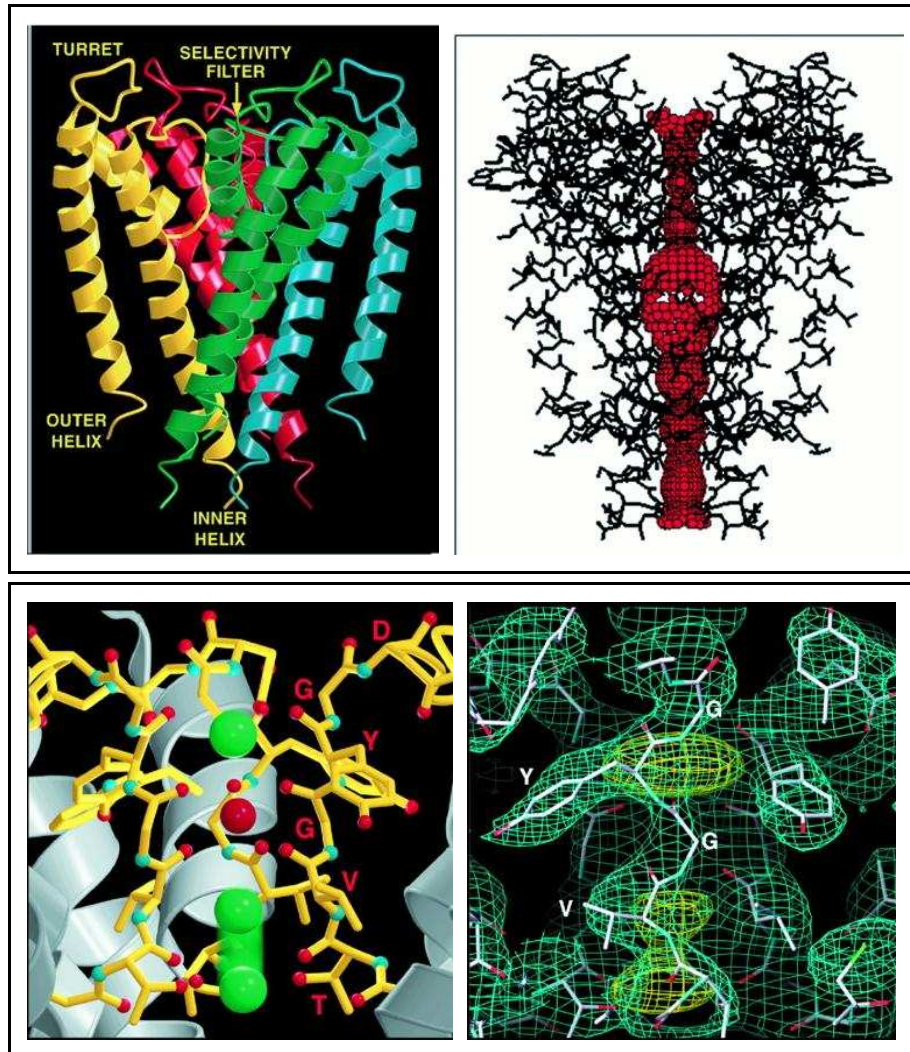
Mixed boundary conditions



double layer (DL) geometry: PBC in x and y dimensions, confined by walls in z dimension

- PBC is applied in dimensions where the system is **homogeneous**
- in the dimension of inhomogeneity the system can be confined by walls
- **Inhomogeneous systems:** the fluid at interfaces is in equilibrium with a bulk system.
- The bulk is a part of the simulation cell (far from walls) or specified by a chemical potential (grand

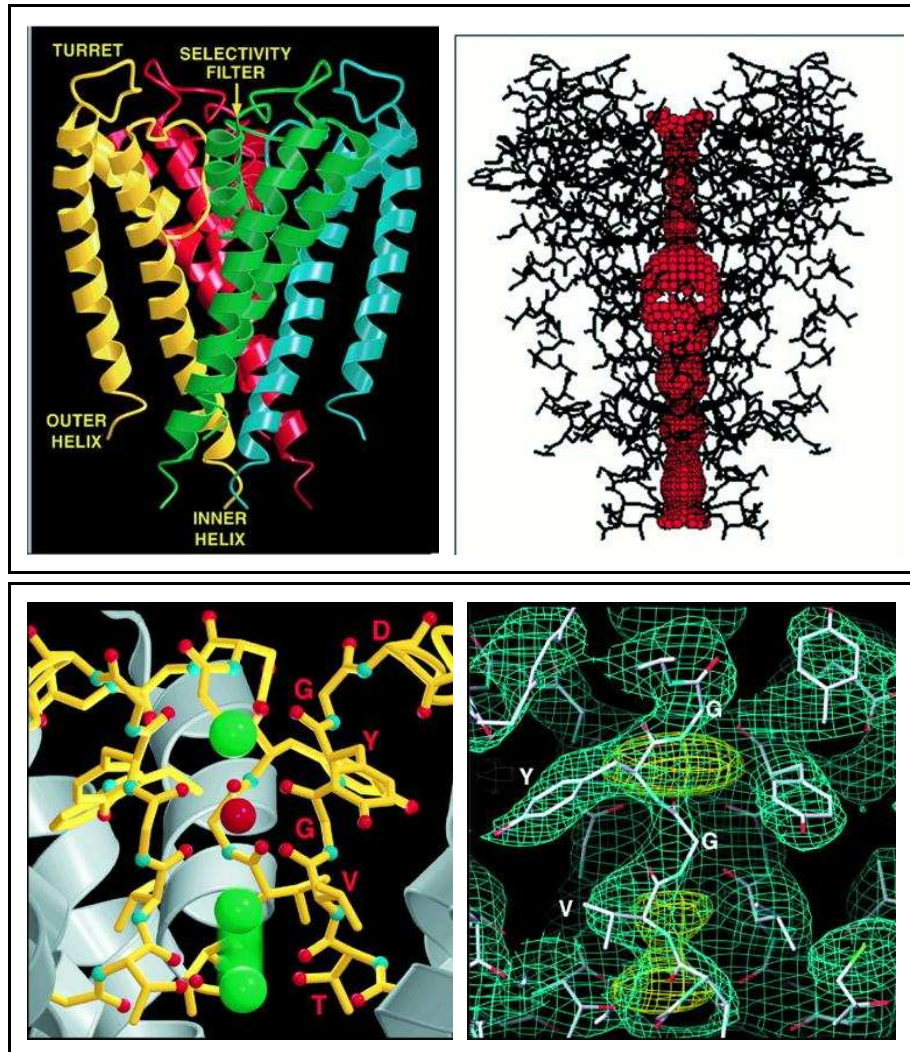
Problems with large scale MD simulations



D. Doyle *et al.*, *Science* 1998, **280**, 69.

- If we know detailed 3D structure of the system (e. g. the KcsA potassium channel on the left), we can perform all atom MD simulation.
- LJ potentials and partial charges on atoms and ions, SPC/E for water.
- **For example:**
T. W. Allen, S. Kuyucak, S. H. Chung:
Molecular dynamics study of the KcsA potassium channel, *Biophysical Journal*, 1999, **77**, 2502.
- **Problems.** At least, in my view.

Problems with large scale MD simulations



D. Doyle *et al.*, *Science* 1998, **280**, 69.

- **Uncertainties of models and molecular parameters** - models and parameters that are good in a given situation might not be good in other situation.
- **Example:** water - some models are good for thermodynamics, others good for dielectric, interfacial, etc. properties.
- results should be verified by comparison to experimental data (current-voltage).
- long enough simulations cannot be run to get a macroscopic sample

Continuum models

Summarized : molecular simulations of systems modelled in full atomic detail **might be problematic**:

- *time consuming* - many particles (macroscopic sampling is not possible)
- *unknown 3D structures* (proteins)
- *uncertainties in estimation of potential parameters*

"Coarse-graining"

- *important* particles are treated explicitly (e. g. ions)
- *the rest* is smoothed into a continuum (e. g. solvent, proteins, membrane, electrode)
- the various components with different polarizabilities are modelled as continuums with different dielectric coefficients
- it can be described by an inhomogeneous dielectric coefficient: $\varepsilon(\mathbf{r})$

Basic task: solving the Poisson equation
$$-\varepsilon_0 \nabla \cdot [\varepsilon(\mathbf{r}) \nabla \psi(\mathbf{r})] = \rho(\mathbf{r})$$

Macroscopic electrostatics

The total charge is split into two parts:

- source (free or explicitly treated) charges: $g(\mathbf{r}) = \rho(\mathbf{r})/\varepsilon_0$ and
- polarization charges $h(\mathbf{r}) = \rho_{pol}(\mathbf{r})/\varepsilon_0$ (**to be determined**)
- constitutive relation: $\rho_{pol}(\mathbf{r}) = -\nabla \cdot \mathbf{P}(\mathbf{r})$, where
- polarization: $\mathbf{P}(\mathbf{r}) = -\varepsilon_0 \chi(\mathbf{r}) \nabla \psi(\mathbf{r})$
- dielectric susceptibility: $\chi(\mathbf{r}) = \varepsilon(\mathbf{r}) - 1$

The corresponding Poisson equation: $\nabla^2 \psi(\mathbf{r}) = -\frac{1}{\varepsilon_0} [\rho(\mathbf{r}) + \rho_{pol}(\mathbf{r})]$

The potential is also split into two parts:

- $\psi(\mathbf{r}) = \psi_e(\mathbf{r}) + \psi_i(\mathbf{r}) = \int_{\mathcal{D}} G(\mathbf{r} - \mathbf{r}') g(\mathbf{r}') d\mathbf{r}' + \int_{\mathcal{D}} G(\mathbf{r} - \mathbf{r}') h(\mathbf{r}') d\mathbf{r}'$
- the Green-function satisfies $\nabla^2 G(\mathbf{r} - \mathbf{r}') = -\delta(\mathbf{r} - \mathbf{r}')$
- $G(\mathbf{r} - \mathbf{r}') = 1/(4\pi|\mathbf{r} - \mathbf{r}'|)$ for the boundary condition $\psi(\mathbf{r}) \rightarrow 0$ if $\mathbf{r} \rightarrow \infty$

Variational formalism

Solution of the Poisson equation minimizes the functional

$$\bullet \quad I[\psi] = \frac{1}{2} \int_{\mathcal{D}} \nabla\psi \cdot \nabla\psi d\mathbf{r} - \int_{\mathcal{D}} \psi \left[g + \frac{1}{2} \nabla \cdot (\chi \nabla\psi) \right] d\mathbf{r}$$

- In minimum the value $-\varepsilon_0 I[\psi]$ is the electrostatic energy
- Substituting the Green function form of $\psi(\mathbf{r})$, the functional can be expressed in terms of the charges: $I[g, h]$
- At a fixed $g(\mathbf{r})$, we have to find $h(\mathbf{r})$ that minimizes $I[g, h]$.
- This is equivalent to minimizing the h -dependent part of the functional $I_2[h]$ for a fixed g .

So, the task is to solve the extremum condition

$$\frac{\delta I_2[h]}{\delta h(\mathbf{r})} = 0$$

- R. Allen, J.-P. Hansen, and S. Melchionna, *Phys. Chem. Chem. Phys.* **3**, 4177 (2001).
- Allen *et al.* solved it with the *steepest descent* method.

Solution of the extremum condition

$$\frac{\delta I_2[h]}{\delta h(\mathbf{r})} = 0$$

We present a different solution resulting in a matrix equation. **The following integral equation can be obtained from the extremum condition:**

$$\begin{aligned} h(\mathbf{r})\varepsilon(\mathbf{r}) - \int_{\mathcal{D}} h(\mathbf{r}') \nabla_{\mathbf{r}} \varepsilon(\mathbf{r}) \cdot \nabla_{\mathbf{r}} G(\mathbf{r} - \mathbf{r}') d\mathbf{r}' \\ = \nabla_{\mathbf{r}} \varepsilon(\mathbf{r}) \cdot \nabla_{\mathbf{r}} \psi_e(\mathbf{r}) - \frac{1}{\varepsilon_0} [\varepsilon(\mathbf{r}) - 1] \rho(\mathbf{r}) \end{aligned}$$

- This equation should be discretized and solved for h .
- It is **general** and valid for arbitrary $\varepsilon(\mathbf{r})$ and $\rho(\mathbf{r})$.
- We can make our life easier by making some assumptions for $\varepsilon(\mathbf{r})$ and $\rho(\mathbf{r})$.

D. Boda, D. Gillespie, W. Nonner, D. Henderson, B. Eisenberg, *Phys. Rev. E* 2004, **69**, 046702.

Point charges as source charges

- Suppose that the source charges are point charges:

$$\rho(\mathbf{r}) = \sum_k z_k e \delta(\mathbf{r} - \mathbf{r}_k)$$

- Polarization charges of magnitude $-z_k e \frac{\varepsilon(\mathbf{r}_k) - 1}{\varepsilon(\mathbf{r}_k)} \delta(\mathbf{r} - \mathbf{r}_k)$ are induced around the point charges (localized on them).

- The electric potential produced by the point charges **and** the polarization charges induced on them:

$$\psi_e(\mathbf{r}) = \frac{e}{4\pi\varepsilon_0} \sum_k \frac{z_k}{\varepsilon(\mathbf{r}_k) |\mathbf{r} - \mathbf{r}_k|}$$

where $\varepsilon(\mathbf{r}_k)$ is the dielectric coefficient at the position of the k th source charge.

- From now on, $h(\mathbf{r})$ denotes **only** the polarization charges induced on the dielectric interfaces. In this case, the basic equation reduces to :

$$h(\mathbf{r})\varepsilon(\mathbf{r}) - \int_{\mathcal{D}} h(\mathbf{r}') \nabla_{\mathbf{r}} \varepsilon(\mathbf{r}) \cdot \nabla_{\mathbf{r}} G(\mathbf{r} - \mathbf{r}') d\mathbf{r}' = \nabla_{\mathbf{r}} \varepsilon(\mathbf{r}) \cdot \nabla_{\mathbf{r}} \psi_e(\mathbf{r})$$

- This is valid for arbitrary $\varepsilon(\mathbf{r})$.

Sharp dielectric interfaces

- When the dielectric is piecewise uniform, $\varepsilon(\mathbf{r})$ jumps from one value to another along a boundary.
- In this case, the volume integrals over \mathcal{D} become surface integrals over the dielectric boundary surfaces \mathcal{B} .
- The basic equation then reduces to:

$$h(\mathbf{s})\varepsilon(\mathbf{s}) - \Delta\varepsilon(\mathbf{s}) \int_{\mathcal{B}} h(\mathbf{s}') \nabla_{\mathbf{s}} G(\mathbf{s} - \mathbf{s}') \cdot \mathbf{n}(\mathbf{s}) d\mathbf{s}' = \Delta\varepsilon(\mathbf{s}) \nabla\psi_e(\mathbf{s}) \cdot \mathbf{n}(\mathbf{s})$$

where

- $h(\mathbf{s})$ is now surface charge distribution
- $\varepsilon(\mathbf{s})$ is the mean average of the dielectric constants on the two sides of the surface
- $\Delta\varepsilon(\mathbf{s})$ is their difference, and
- $\mathbf{n}(\mathbf{s})$ is a normal vector of the surface

The matrix equation

The previous equation is valid for any discrete value of \mathbf{s}_α . Use the notations

- normal vector: $\mathbf{n}_\alpha = \mathbf{n}(\mathbf{s}_\alpha)$
- mean dielectric constant: $\varepsilon_\alpha = \varepsilon(\mathbf{s}_\alpha)$
- jump in the dielectric constant: $\Delta\varepsilon_\alpha = \Delta\varepsilon(\mathbf{s}_\alpha)$

The surface \mathcal{B} is discretized into surface elements. Let us suppose that the induced surface charge is constant on surface element β denoted by h_β . Then our equation becomes

$$\sum_{\beta} h_{\beta} \left[\varepsilon_{\beta} \delta_{\alpha\beta} - \Delta\varepsilon_{\alpha} \int_{a_{\beta}} \nabla_{\mathbf{s}_{\alpha}} G(\mathbf{s}_{\alpha} - \mathbf{s}_{\beta}) \cdot \mathbf{n}_{\alpha} d\mathbf{s}_{\beta} \right] = \Delta\varepsilon_{\alpha} \nabla\psi_e(\mathbf{s}_{\alpha}) \cdot \mathbf{n}_{\alpha}.$$

where the integral expresses the polarization of the surface element β by the induced charge at \mathbf{s}_α , and vice versa. The integral is taken for the β th surface element.

The matrix equation

If \mathbf{s}_α is the center of the α th surface element, the previous equation can be written in the matrix form: $\mathbf{A}\mathbf{h} = \mathbf{c}$, where

- the $A_{\alpha\beta} = \varepsilon_\beta \delta_{\alpha\beta} - \Delta\varepsilon_\alpha \int_{a_\beta} \nabla_{\mathbf{s}_\alpha} G(\mathbf{s}_\alpha - \mathbf{s}_\beta) \cdot \mathbf{n}_\alpha d\mathbf{s}_\beta$ matrix depends only on the geometry of the dielectric
- \mathbf{h} is the vector of induced charges
- $c_\alpha = \Delta\varepsilon_\alpha \nabla\psi_e(\mathbf{s}_\alpha) \cdot \mathbf{n}_\alpha$ depends on the source charges
- If the geometry does not change in a simulation, the matrix need be inverted only once at the beginning of the simulation.
- Moving the source charges (the ions) changes the vector \mathbf{c} , from which the induced charges are calculated by the matrix-vector multiplication $\mathbf{h} = A^{-1}\mathbf{c}$.

Calculation of the integral

Regarding the calculation of the integral $I_{\alpha\beta} = \int_{a_\beta} \nabla_{\mathbf{s}_\alpha} G(\mathbf{s}_\alpha - \mathbf{s}_\beta) \cdot \mathbf{n}_\alpha d\mathbf{s}_\beta$ there are two approaches

1. Treating the surface charge h_β as a **point charge** of magnitude $h_\beta a_\beta$ at the center of the β th surface element of area a_β

$$I_{\alpha\beta} = \nabla_{\mathbf{s}_\alpha} G(\mathbf{s}_\alpha - \mathbf{s}_\beta) \cdot \mathbf{n}_\alpha a_\beta$$

for $\beta \neq \alpha$ and 0 otherwise [Boda *et al.*, *Phys. Rev. E*, 2004, **69**, 046702.]. This matrix has been developed before from the boundary condition $D_{1n} = D_{2n}$, $E_{1t} = E_{2t}$. [Hoshi *et al.* *JCP*, 1987; Lu and Green, *PCPS*, 1997]

2. Treating h_β as a constant **surface charge** over the β th surface element, and calculating $I_{\alpha\beta}$ numerically after an appropriate parametrization of the surface [Nonner and Gillespie, *Biophys. J.* in preparation]. This approach is especially important if the surface is curved, therefore, we use the name *curvature correction*.

Calculation of the energy

- The **source charge - source charge** interaction energy:

$$W_e = \frac{1}{2} \sum_j e z_j \psi_e(\mathbf{r}_j)$$

- The **source charge - induced charge** interaction energy:

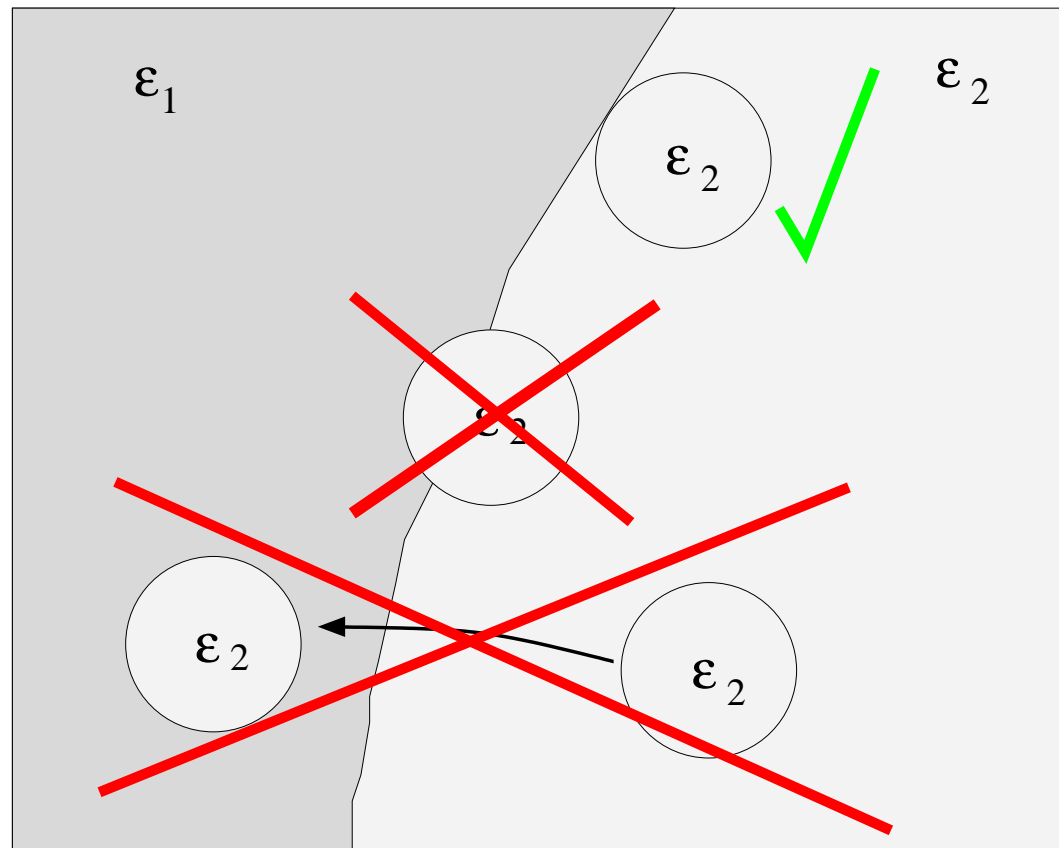
$$W_i = \frac{e}{8\pi} \sum_j z_j \sum_{\beta} h_{\beta} \int_{a_{\beta}} \frac{ds}{|\mathbf{s} - \mathbf{r}_j|}$$

Similarly to the calculation of the integral $I_{\alpha\beta}$, this energy can also be calculated on two levels of approximation:

1. Treating the induced charge as a **point charge** of magnitude $h_{\beta}a_{\beta}$, the integral in the above equation becomes $\frac{a_{\beta}}{|\mathbf{s}_{\beta} - \mathbf{r}_j|}$.
2. Treating the induced charge as a **surface charge** with the constant value h_{β} over the β th surface element, the integral should be calculated numerically. This is a time consuming step in a simulation because the $|\mathbf{s} - \mathbf{r}_j|$ distances have to be evaluated once the j th ion is displaced.

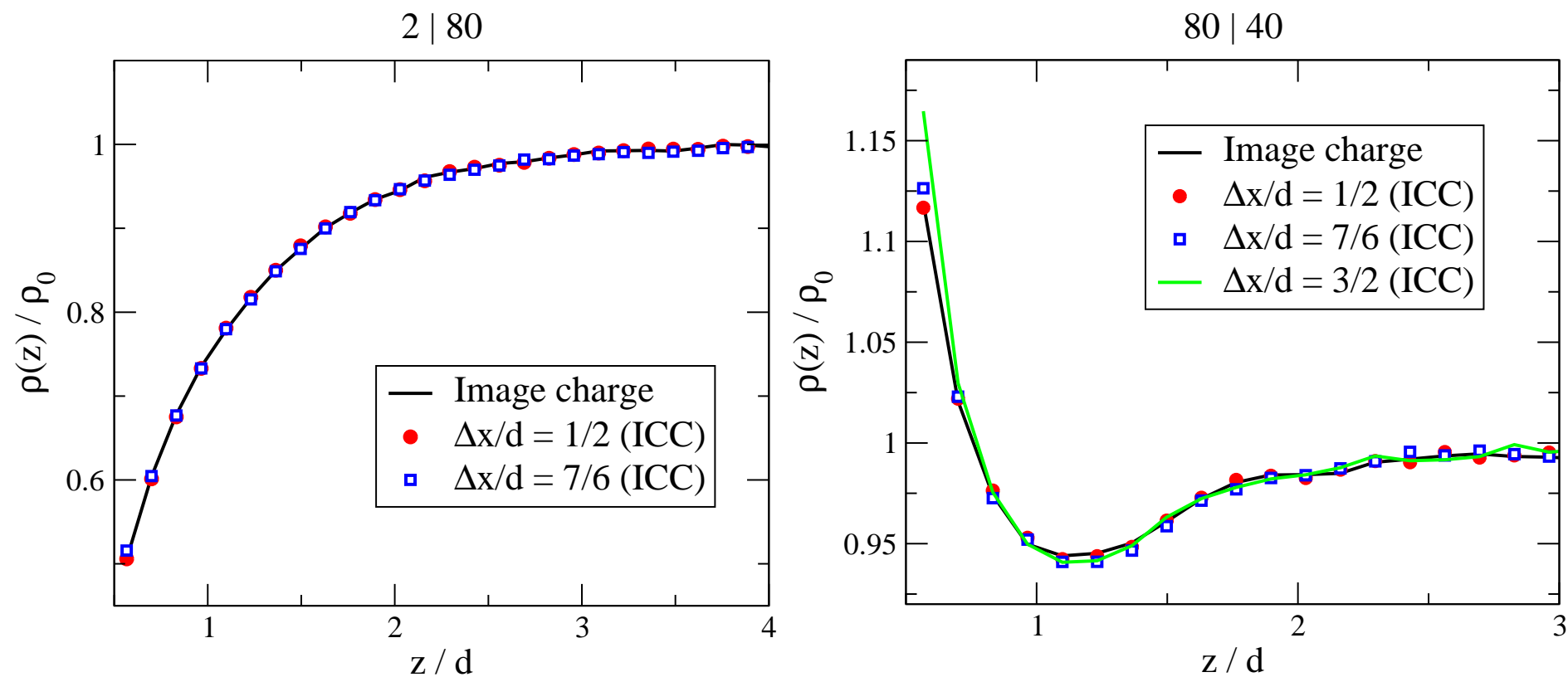
Ion is modelled as a hard sphere with a point charge in the center

- The dielectric constant inside the hard spheres is the same as outside.
- The ions cannot overlap with the dielectric boundaries and cannot leave their host dielectric.
- Otherwise, new dielectric boundaries would appear - matrix A should be inverted again.



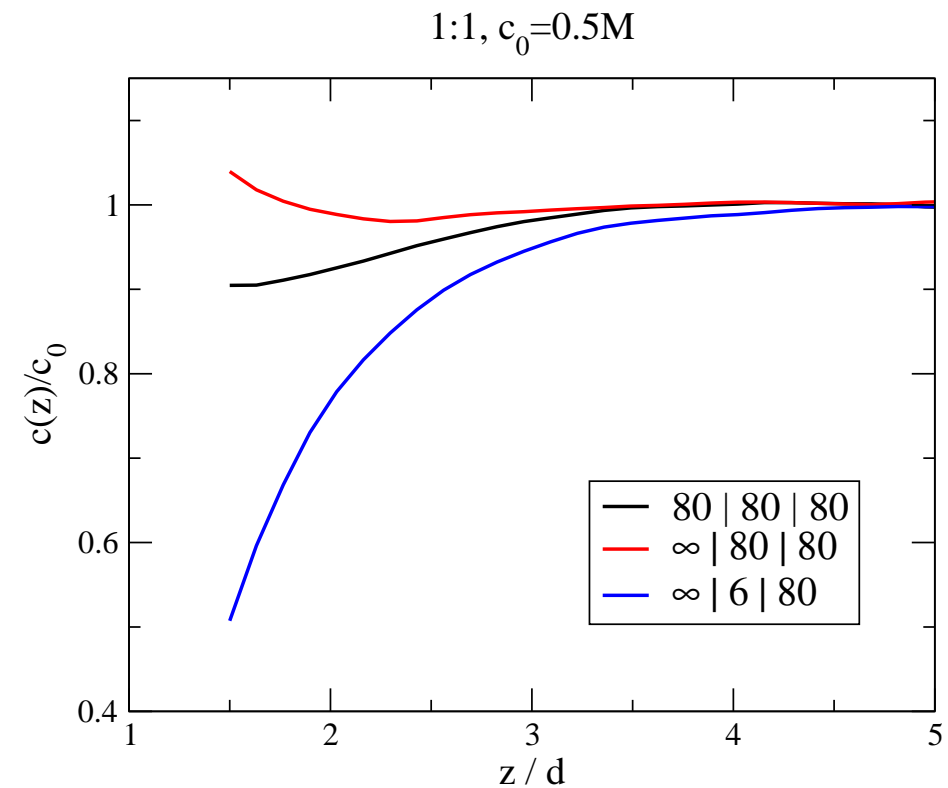
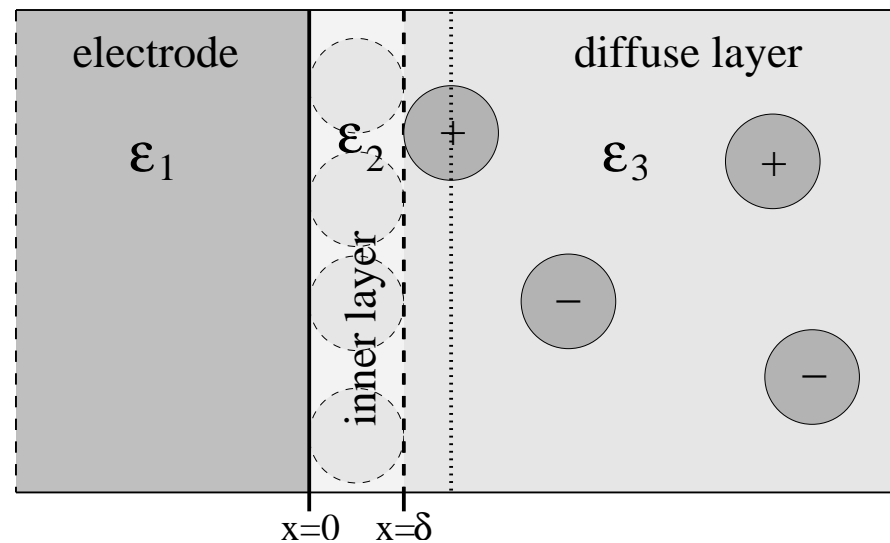
One flat interface: $\varepsilon_1|\varepsilon_2$ geometry - ions on the right side

Comparison of density profiles obtained from the ICC and the image charge method for various resolutions of the grid. [Boda *et al. PRE*, 2004, **69**, 046702.]



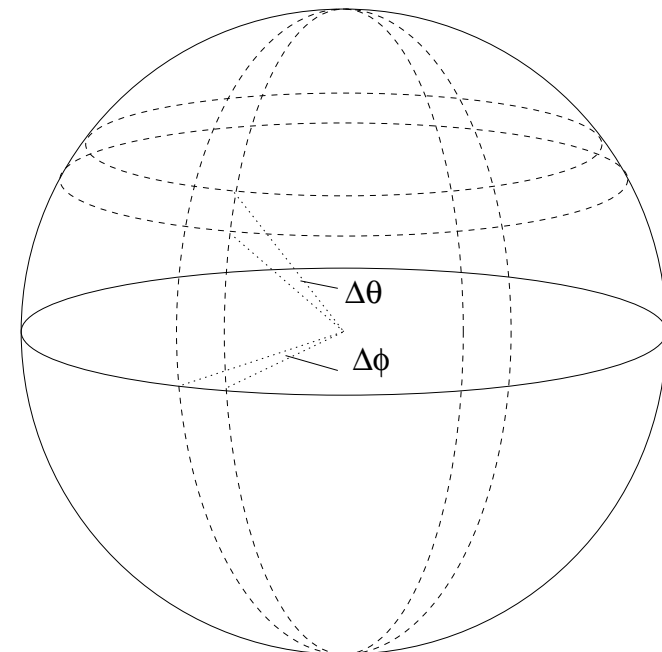
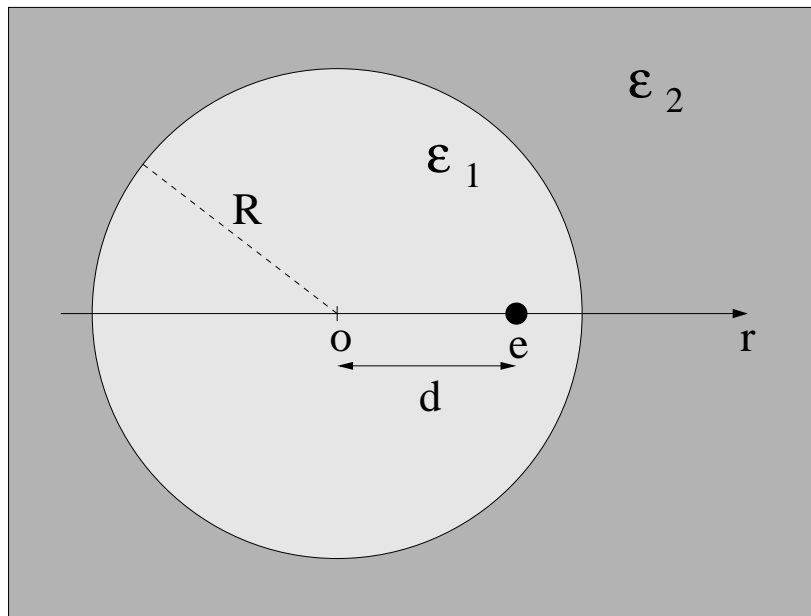
Two flat interfaces: $\epsilon_1|\epsilon_2|\epsilon_3$ geometry - electrical double layer

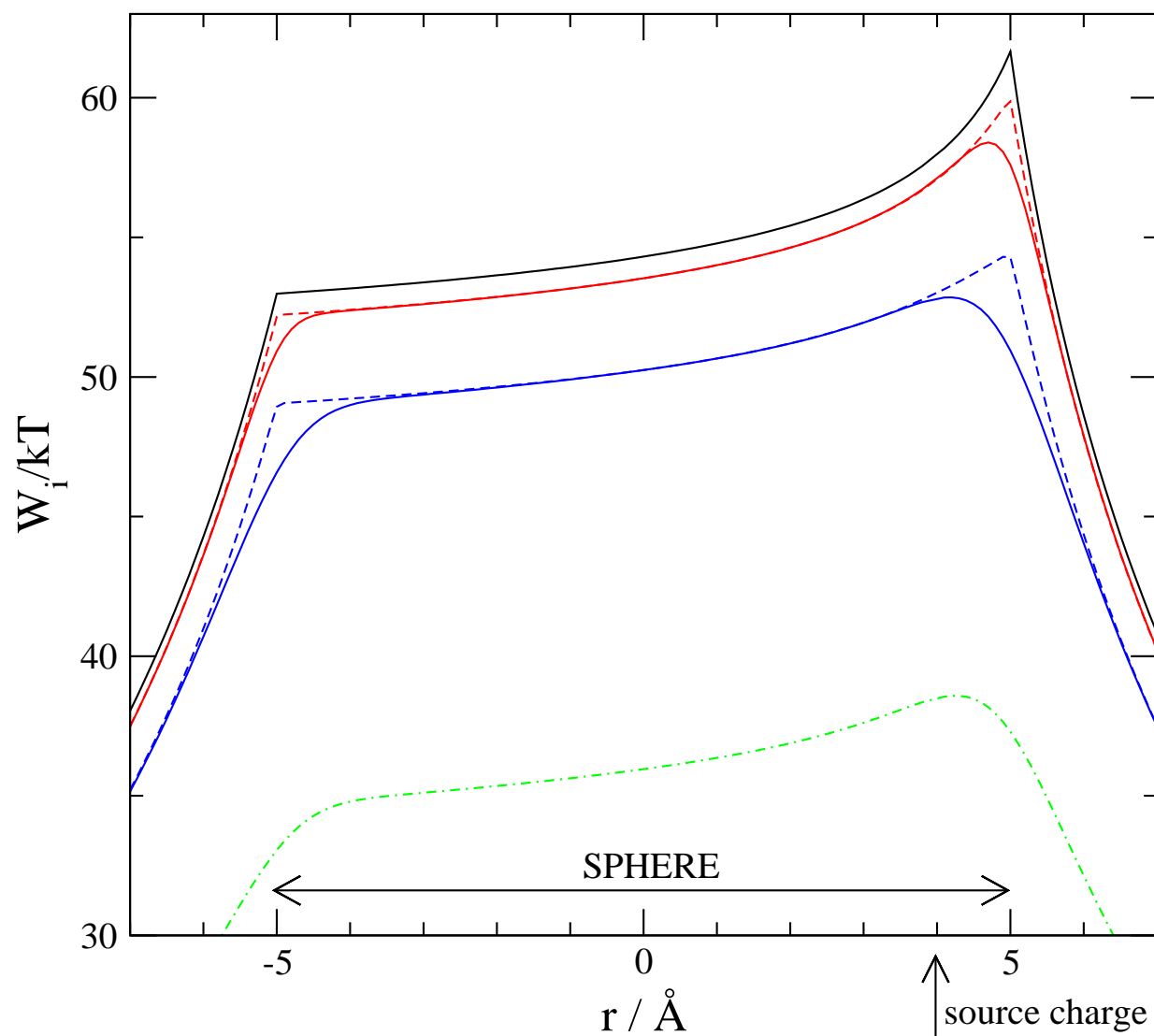
It is usual to assume that the inner layer has a dielectric constant different from that of the diffuse layer or the electrode because of the need for empirical adjustments to obtain agreement with experiments. The electrostatic consistency of the approach should be studied.



A dielectric sphere $\epsilon_1 = 80$ embedded in a dielectric $\epsilon_2 = 2$

- Radius of the sphere: $R = 5 \text{ \AA}$.
- Distance of a source charge e from the center of the sphere: $d = 4 \text{ \AA}$
- Grid: spherical coordinates ϑ and ϕ evenly divided into intervals $\Delta\theta = \Delta\phi$, N is the number of surface elements.
- Analytic solution: series in terms of Legendre polynomials.





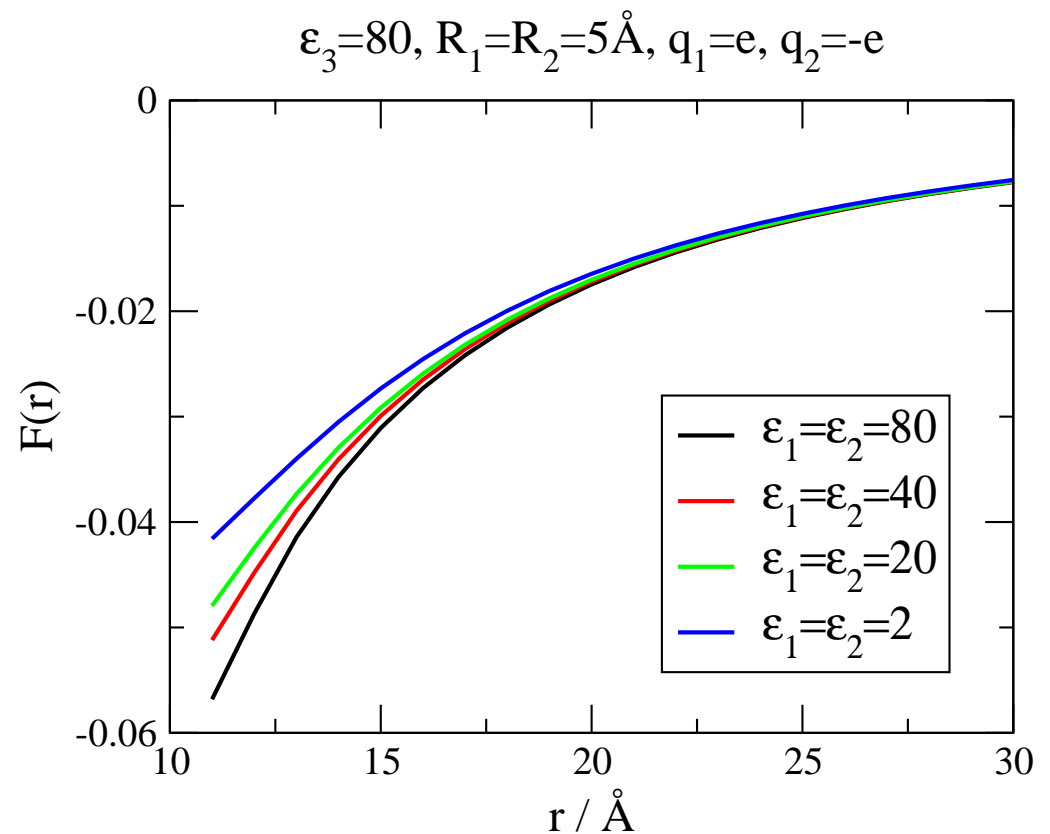
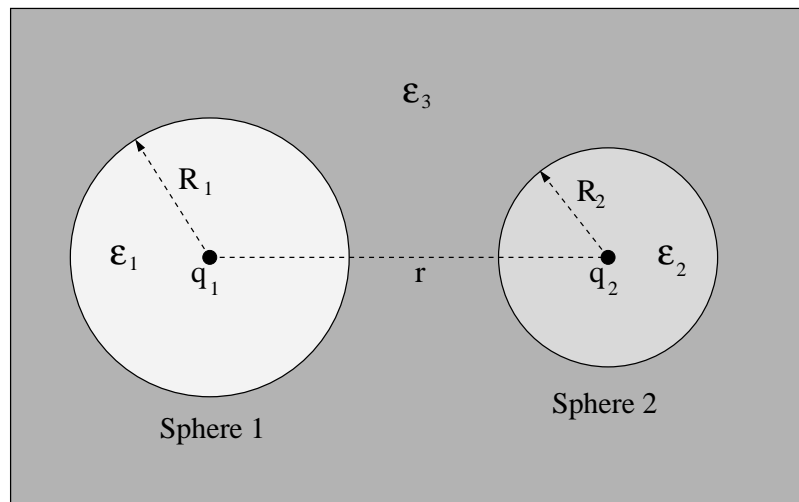
Source charge - induced charge energy as a function of the distance from the center of the sphere along the line on the charge and the sphere center

— Analytic
 Red: $N=512$
 Blue: $N=128$
 Solid: approach 2 for $I_{\alpha\beta}$
 but approach 1 for W_i
 Dashed: approach 2 for both $I_{\alpha\beta}$
 and W_i
 - · - approach 1 for both $I_{\alpha\beta}$
 and W_i , $N=2048$ (!!!)

The *curvature correction* is important!!!

The effective force acting between two charged dielectric spheres

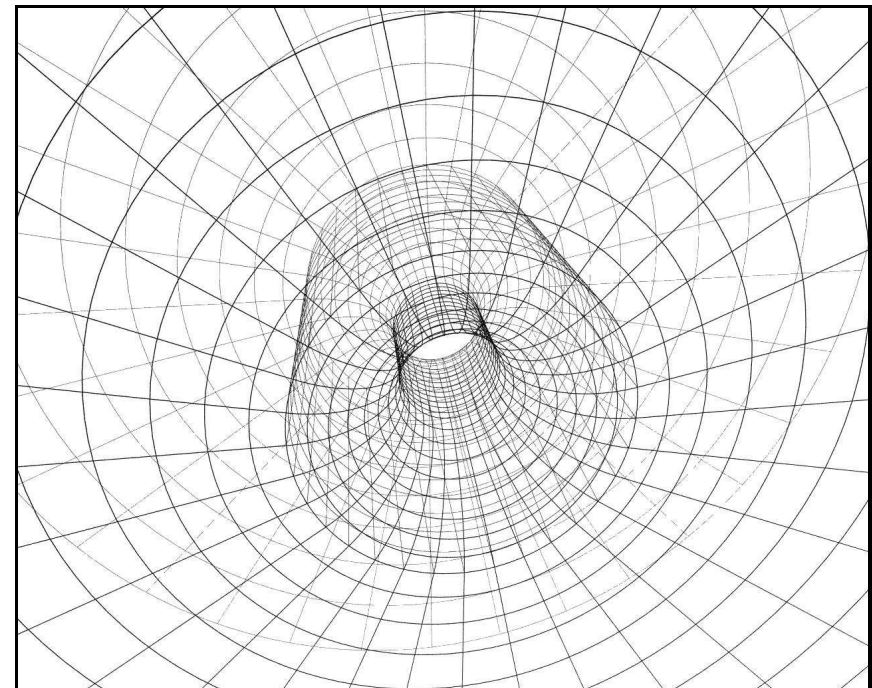
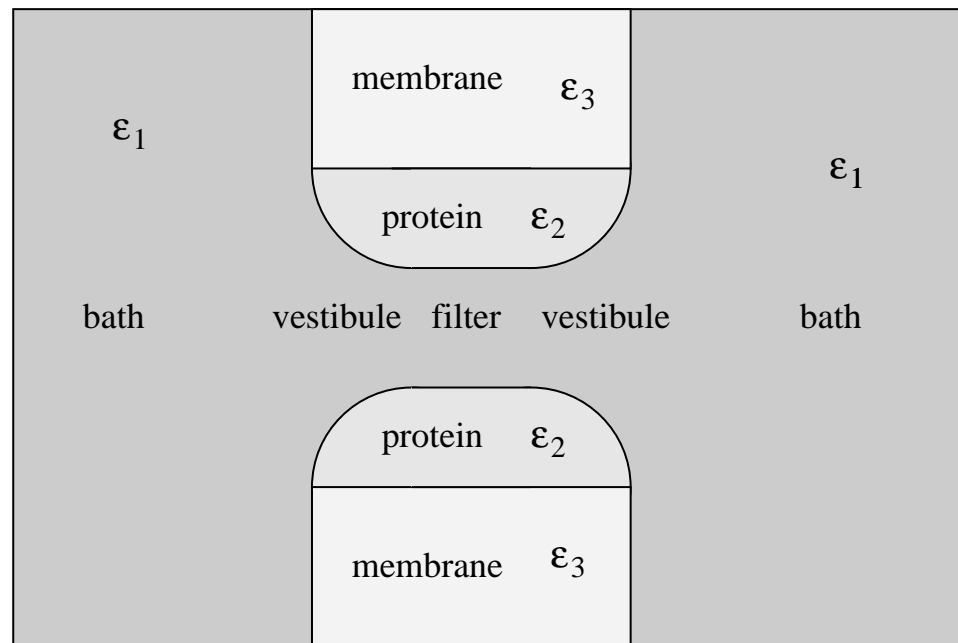
The effective pair potential is defined as $\varphi(r) = W(r) - W(r \rightarrow \infty)$. The energy $W(r \rightarrow \infty)$ corresponds to the interaction energy between the charge and the induced charge on its own sphere. The effective force is $F(r) = -d\varphi(r)/dr$.



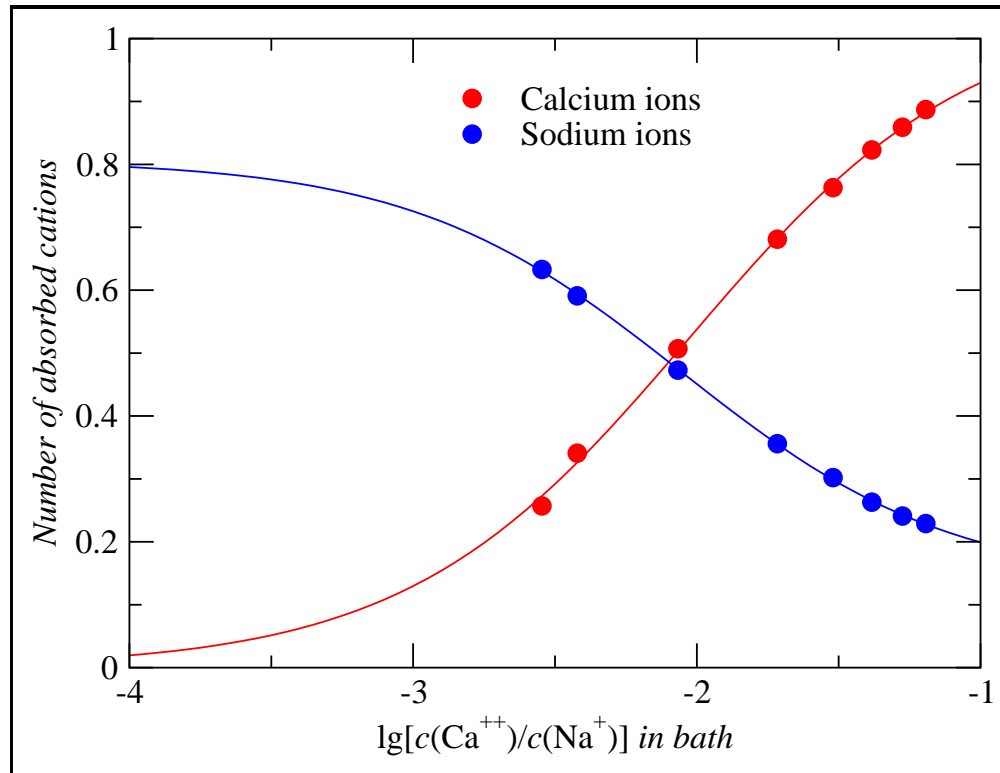
MC simulation for a model calcium channel

The selectivity filter of the calcium channel is known to be lined by 4 glutamate groups (EEEE locus). They are represented by 8 half charged oxygen ions that are confined to the filter but can move freely inside. A 0.1M NaCl solution used and a few Ca^{++} ions.

Question: whether the Na^+ or the Ca^{++} enters the filter with a higher probability?



MC simulation for a model calcium channel

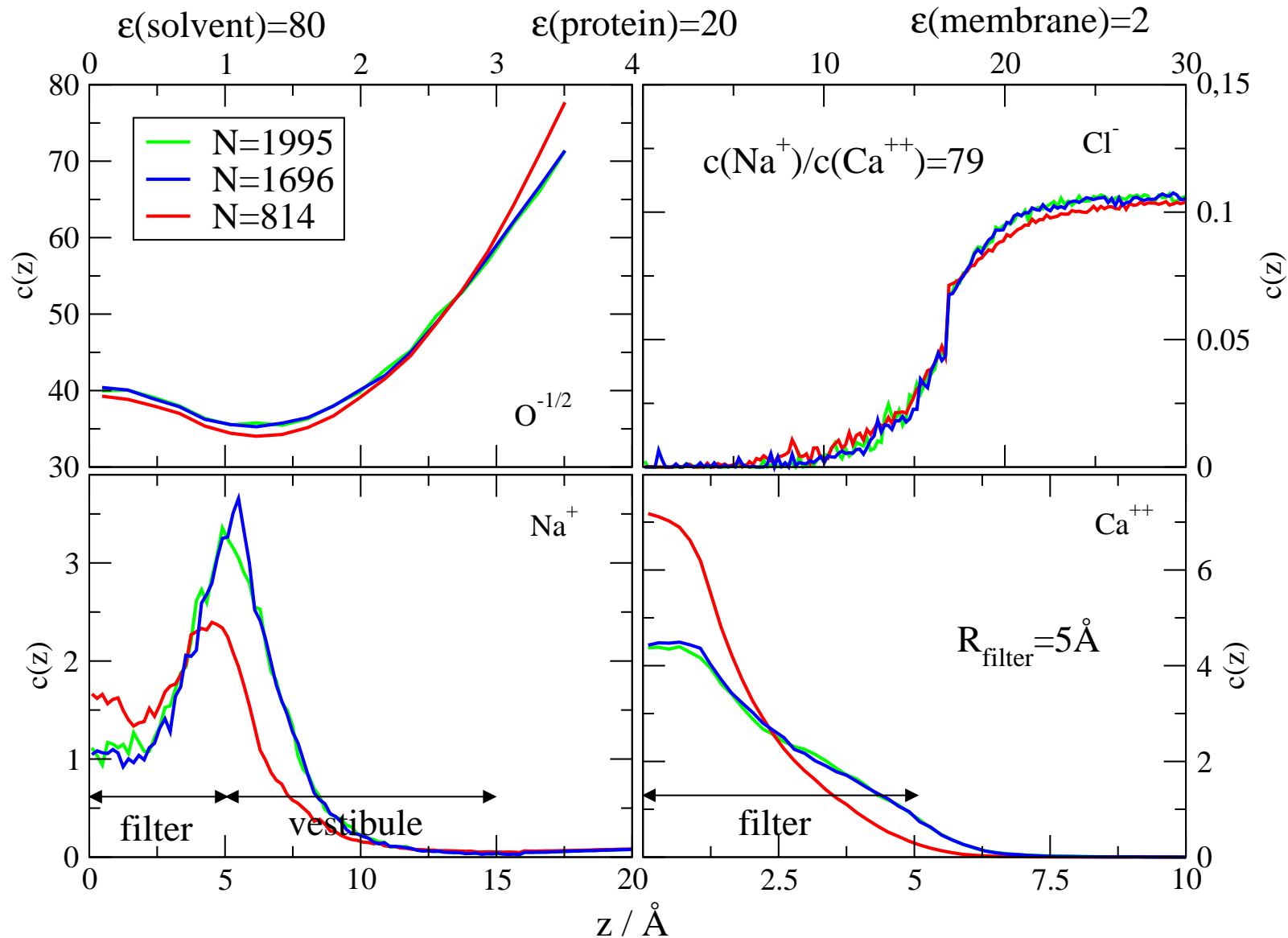


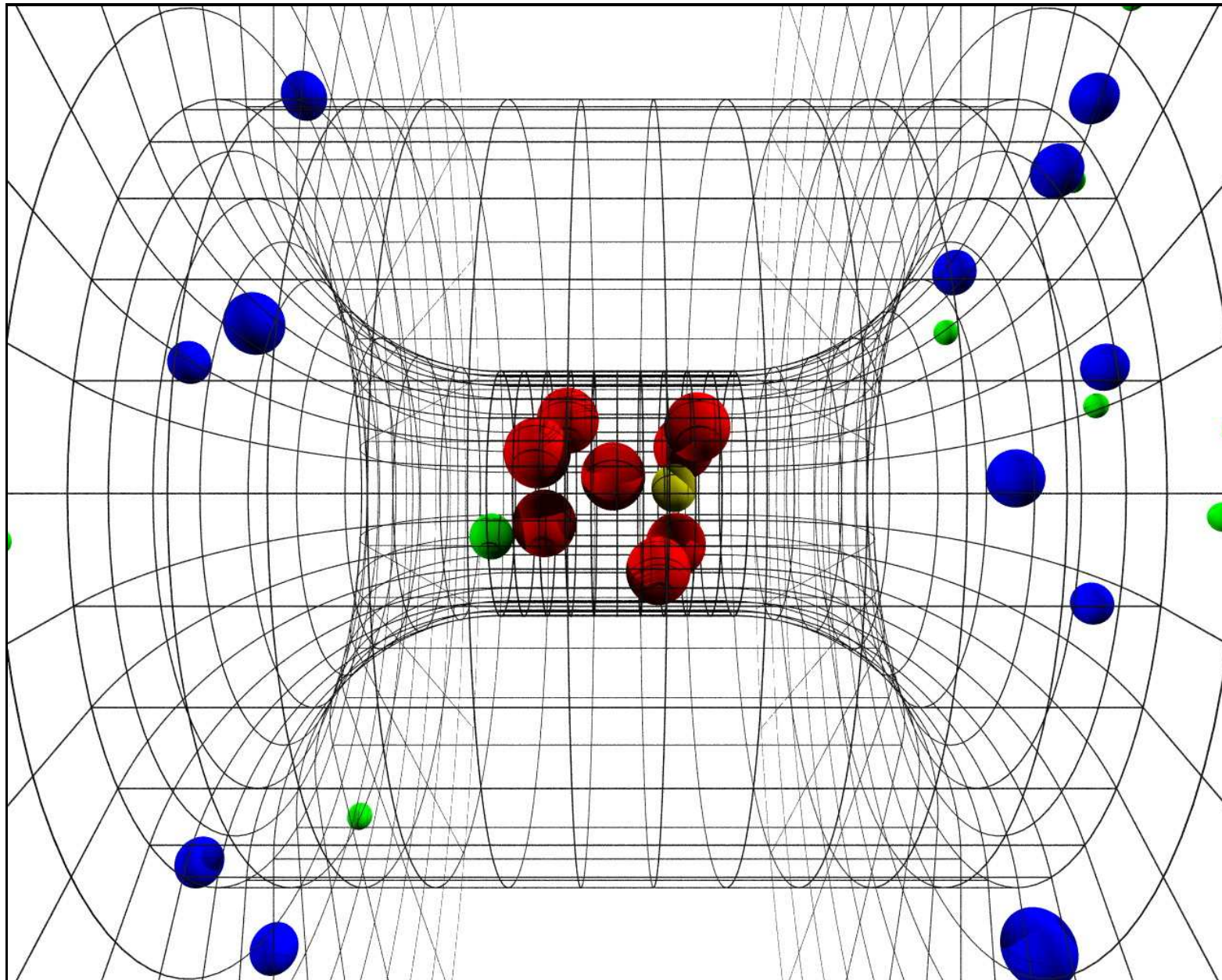
Results for uniform dielectric constant -
 $\varepsilon = 78.5$ everywhere, no vestibule.

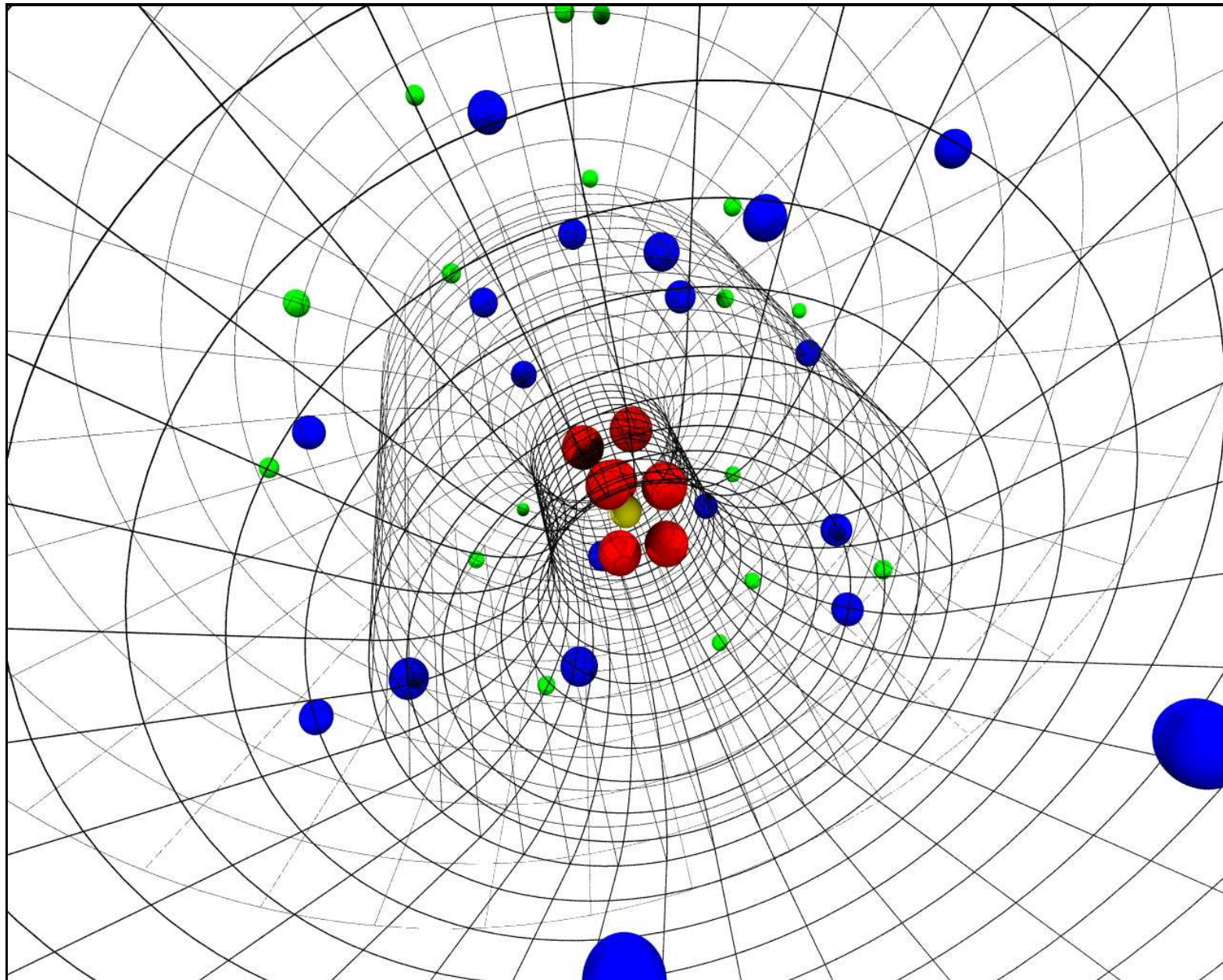
D. Boda et al., Molec. Phys., 2002 **100**, 2361.

- The concentration of sodium ions is kept constant in the bath at 0.1 M. CaCl_2 is added to the system.
- The calcium ions replace sodium ions even when their bath concentration is 0.01 times smaller than that of the sodium ions.
- **Explanation:** *charge-space competition* (CSC) mechanism
- The calcium ions provide two times the charge to neutralize the glutamate groups than sodium ions using about the same volume.

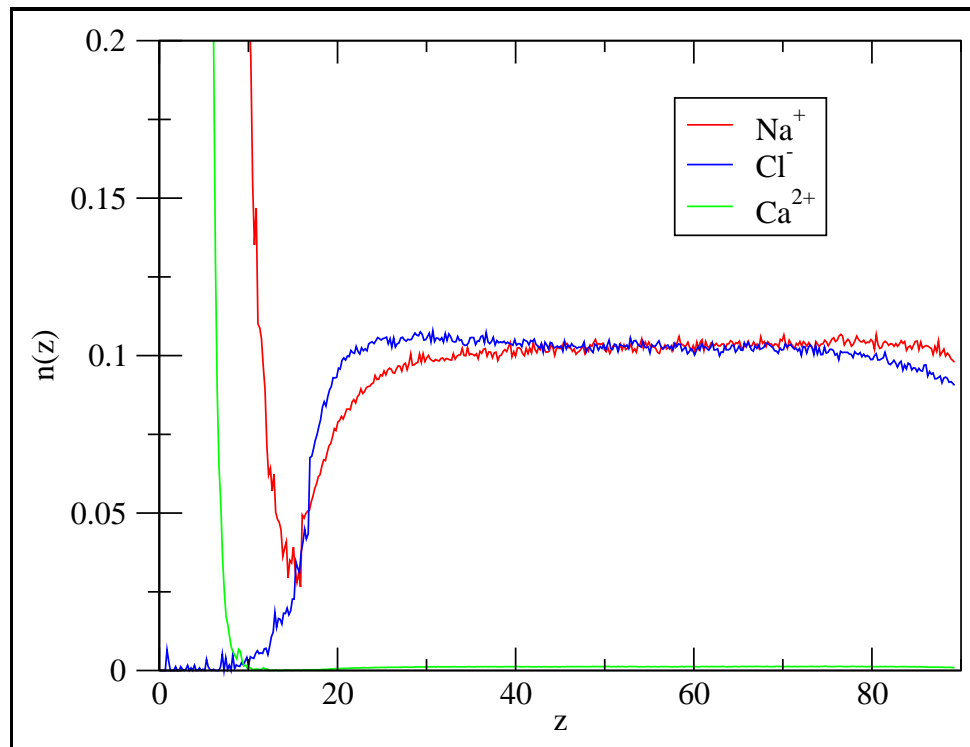
Preliminary results for inhomogeneous dielectric







Problem of absence of charge neutral bulk

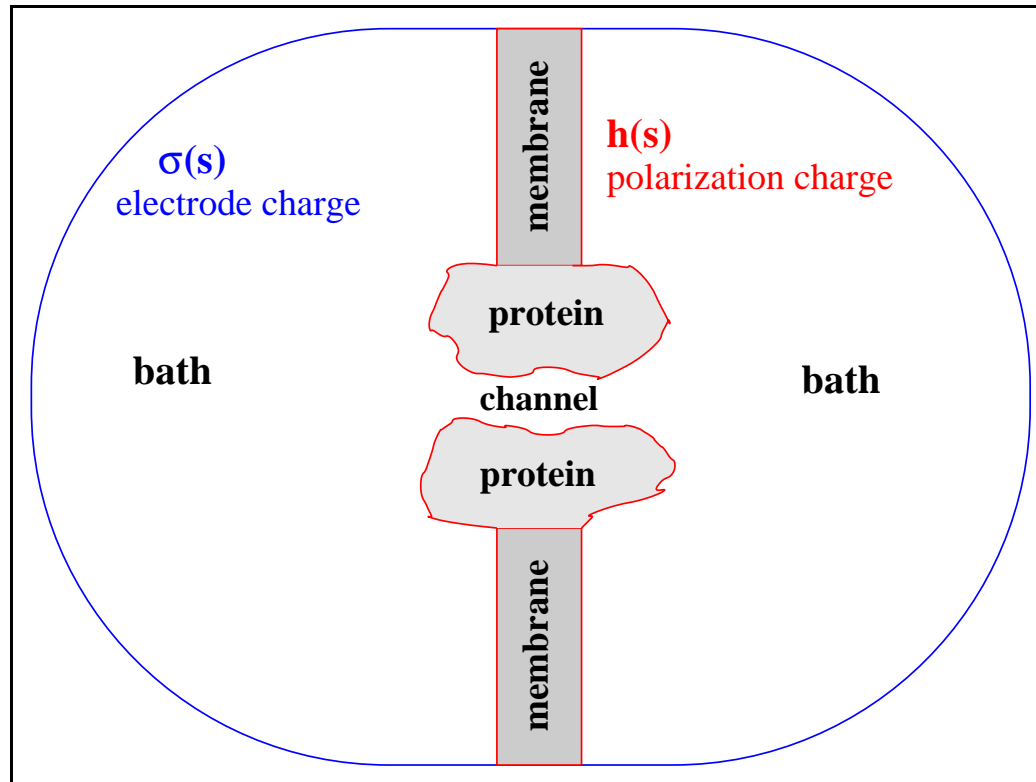


The previous figure with a different scale showing the bulk. There is **no** an electroneutral bulk.

Explanation:

- “Fixed charge ensemble”
- Normal procedure in **homogeneous** ϵ simulations: the number of ions is chosen so that the system is electroneutral.
- The electroneutral bulk is automatically formed far from the walls (inhomogeneities).
- Here, polarization charges are induced on the dielectric boundaries and **prevent** the formation of charge neutral bulk.

Simulation by imposing Dirichlet or Neumann boundary conditions



Idea of Nonner and Gillespie (still in preparation): Define confining surface of the system (they call it electrode). Apply an appropriate surface charge $\sigma(\mathbf{r})$ on the electrode to fulfill BC.

- **Dirichlet BC:** prescribed potential on the surface: $V(s)$
- **Neumann BC:** prescribed normal electric field on the surface: $E_n(s)$
- As the ions move, both the polarization charge $h(s)$ and the electrode charge $\sigma(s)$ are changing.
- Electrode charge induces polarization charge and vice versa, so their calculation has to be coupled.

Coupling induced and electrode charge calculations

Equation for the dielectric boundaries \mathcal{B} :

$$4\pi \frac{\varepsilon(\mathbf{s})}{\Delta\varepsilon(\mathbf{s})} h(\mathbf{s}) + \int_{\mathcal{B}} h(\mathbf{s}') \frac{(\mathbf{s} - \mathbf{s}') \cdot \mathbf{n}(\mathbf{s})}{|\mathbf{s} - \mathbf{s}'|^3} d\mathbf{s}' + \int_{\mathcal{S}} \sigma(\mathbf{s}') \frac{(\mathbf{s} - \mathbf{s}') \cdot \mathbf{n}(\mathbf{s})}{|\mathbf{s} - \mathbf{s}'|^3} d\mathbf{s}' = - \sum_k q_k \frac{(\mathbf{s} - \mathbf{r}_k) \cdot \mathbf{n}(\mathbf{s})}{\varepsilon(\mathbf{r}_k) |\mathbf{s} - \mathbf{r}_k|^3}$$

Equation for the electrode \mathcal{S} :

$$\int_{\mathcal{B}} \frac{h(\mathbf{s}')}{|\mathbf{s} - \mathbf{s}'|} d\mathbf{s}' + \int_{\mathcal{S}} \frac{\sigma(\mathbf{s}')}{|\mathbf{s} - \mathbf{s}'|} d\mathbf{s}' = 4\pi\varepsilon_0 V(\mathbf{s}) - \sum_k \frac{q_k}{\varepsilon(\mathbf{r}_k) |\mathbf{s} - \mathbf{r}_k|}$$

To solve the problem, both surfaces \mathcal{B} and \mathcal{S} have to be discretized resulting in a matrix equation. *Work is in progress...*

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Thank you for your attention!