

The Induced Charge Computation Method and its Application in Monte Carlo Simulations of Inhomogeneous Dielectric Systems

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Continuum models

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

- $$I[\psi] = \frac{1}{2} \int_{\mathcal{D}} \nabla\psi \cdot \nabla\psi d\mathbf{r} - \int_{\mathcal{D}} \psi \left[g + \frac{1}{2} \nabla \cdot (\chi \nabla\psi) \right] d\mathbf{r}$$
- 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* in press (2004).

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*, in press]. 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:

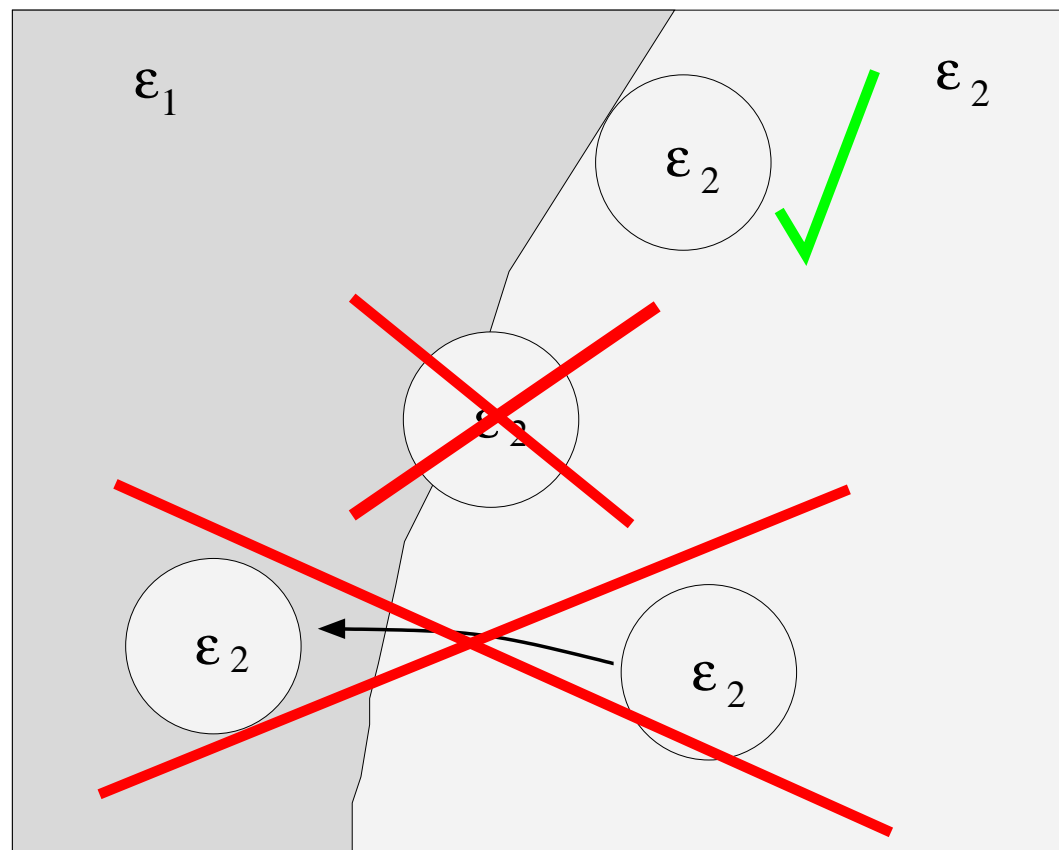
$$W_i = \frac{e}{8\pi} \sum_j z_j \sum_{\beta} h_{\beta} \int_{a_{\beta}} \frac{ds}{|\mathbf{s} - \mathbf{r}_j|}$$

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.

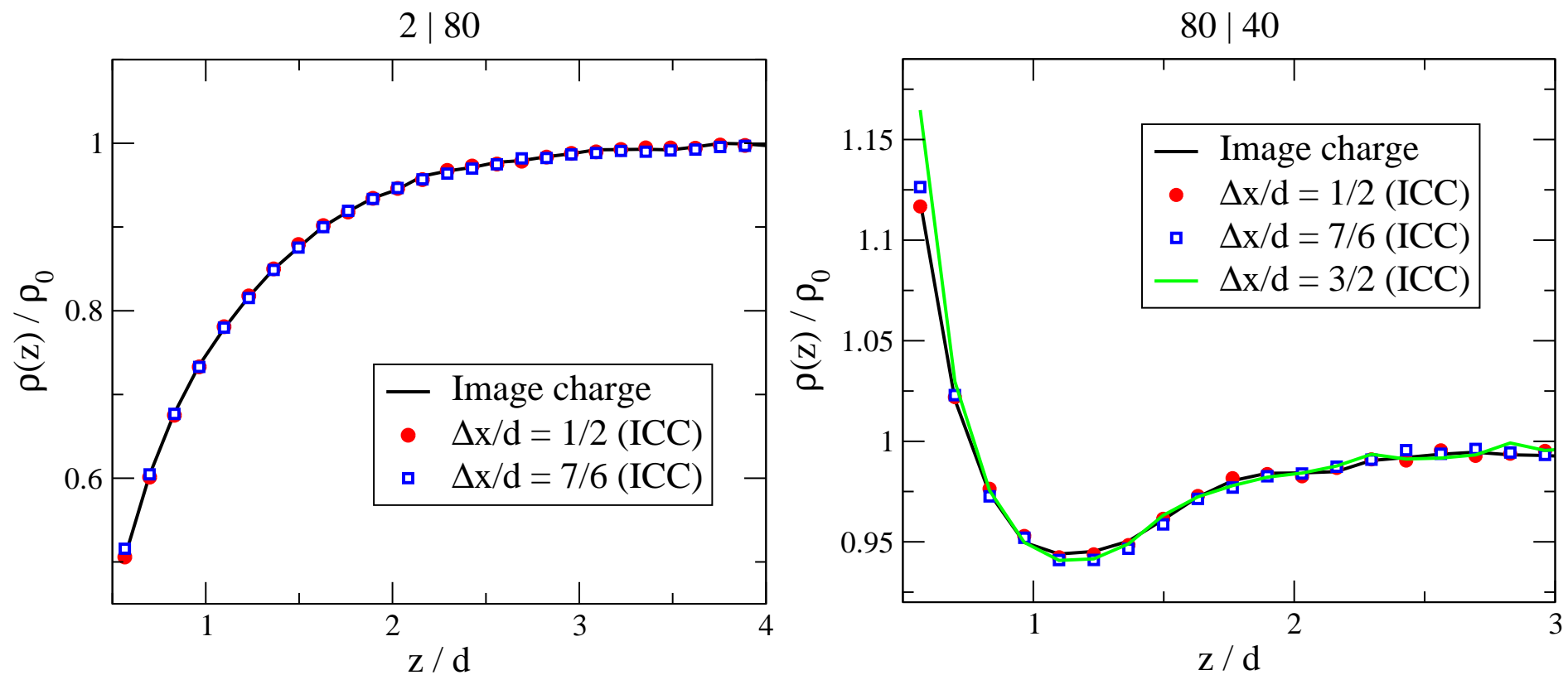
Ion is modelled as a hard sphere with a point charge in the center

- 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.



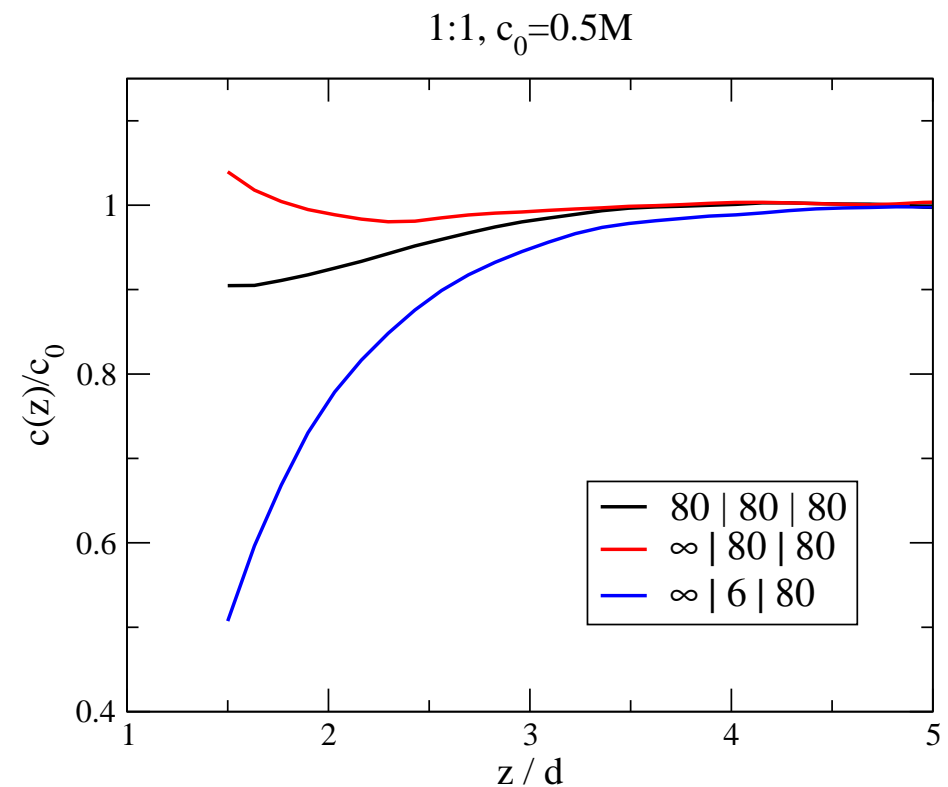
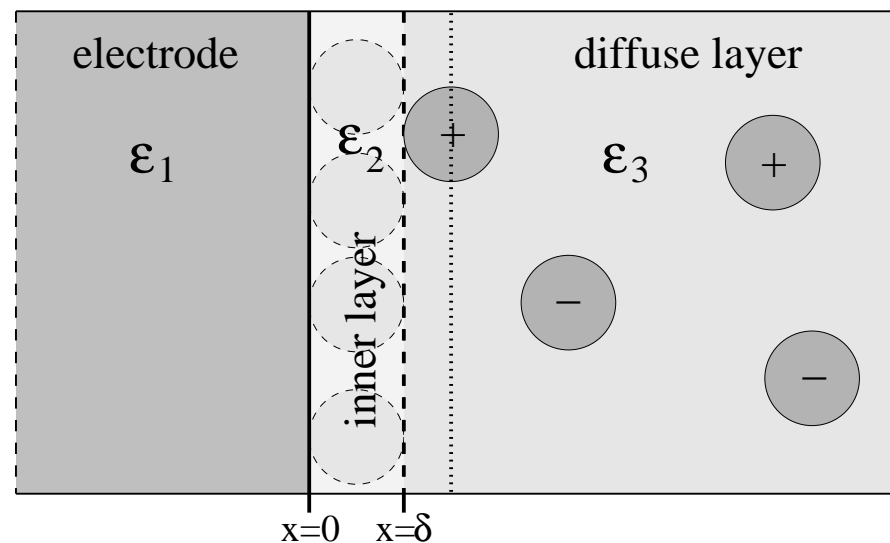
One flat interface: $\varepsilon_1|\varepsilon_2$ geometry - ions on the right side

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



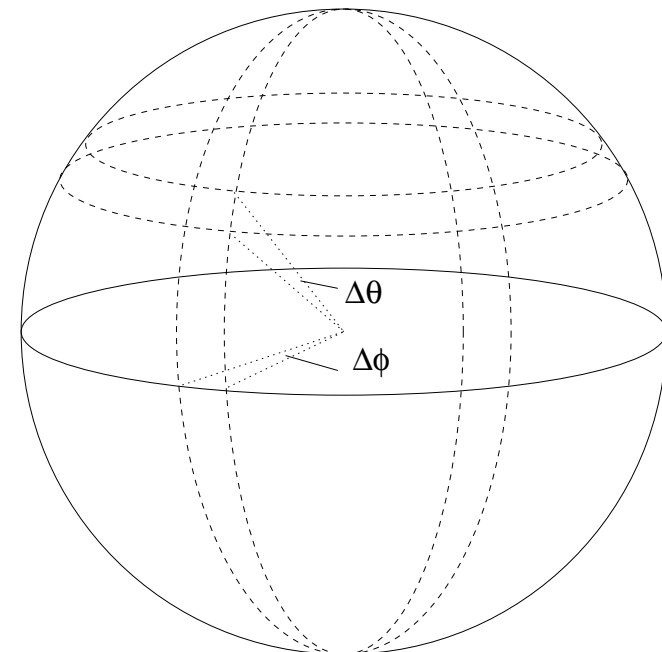
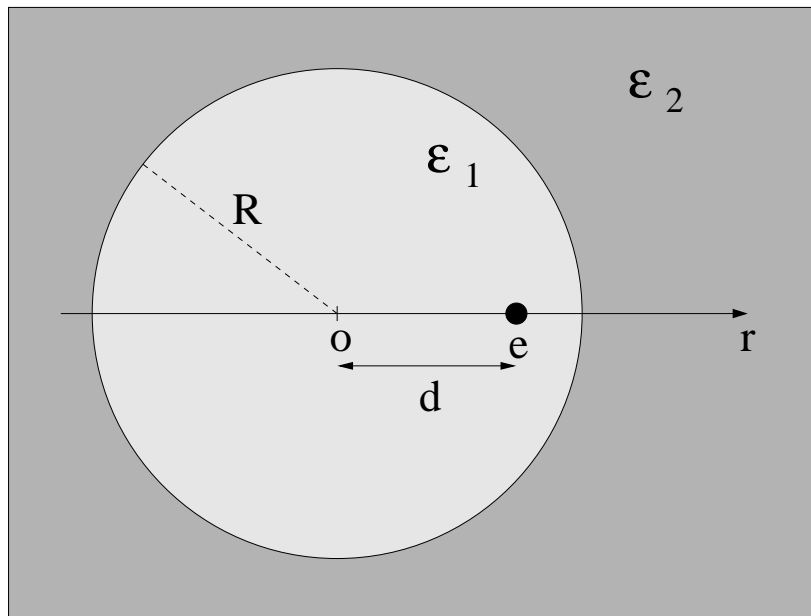
Two flat interfaces: $\epsilon_1|\epsilon_2|\epsilon_3$ geometry - electrical double layer

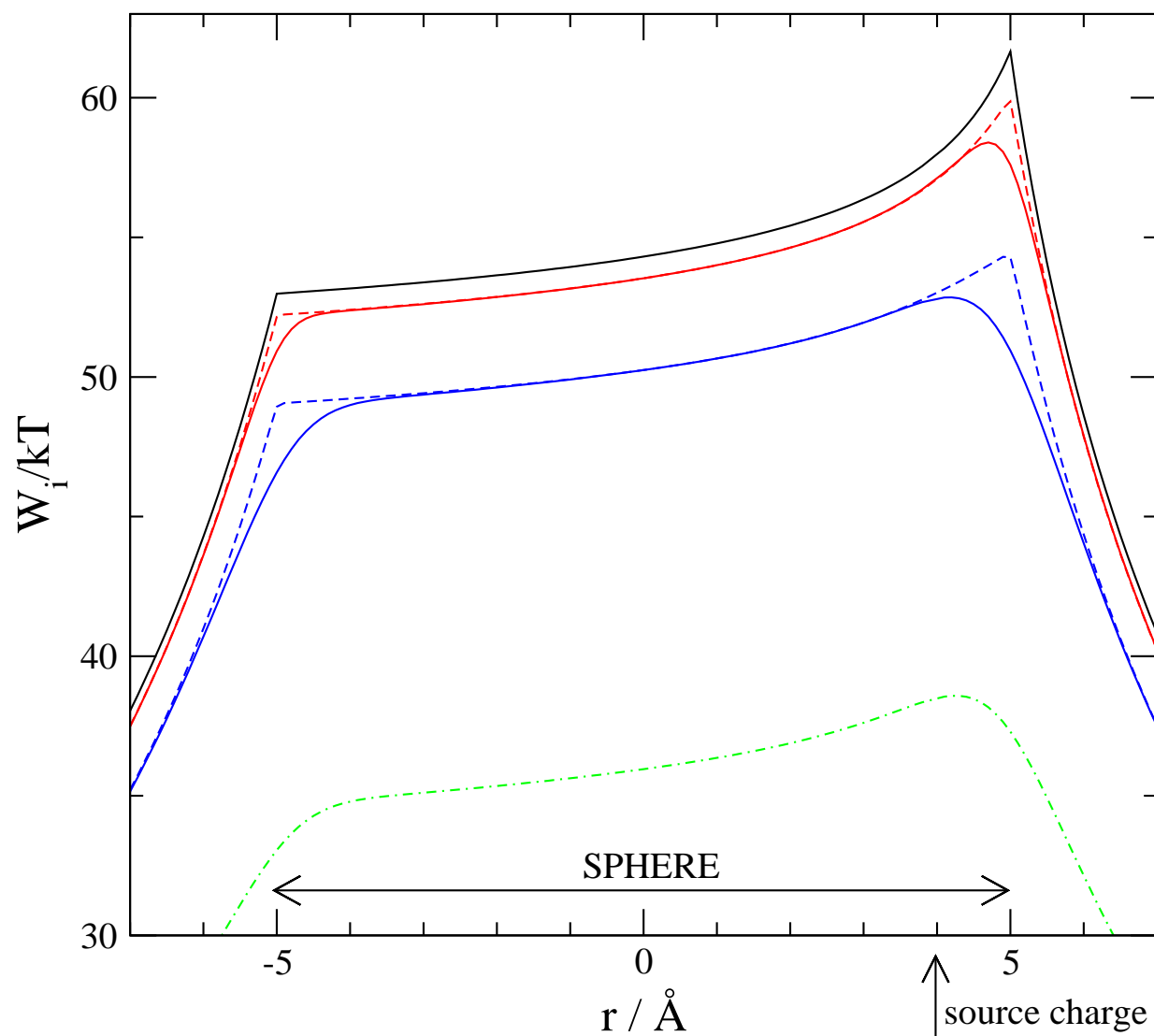
It is usual to assume that the inner layer has a dielectric constant different from that of the diffuse layer or the electrode because of the need for empirical adjustments to obtain agreement with experiments. The electrostatic consistency of the approach should be studied. [Boda, Gillespie, Nagy, and Henderson, JCP, submitted]



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.





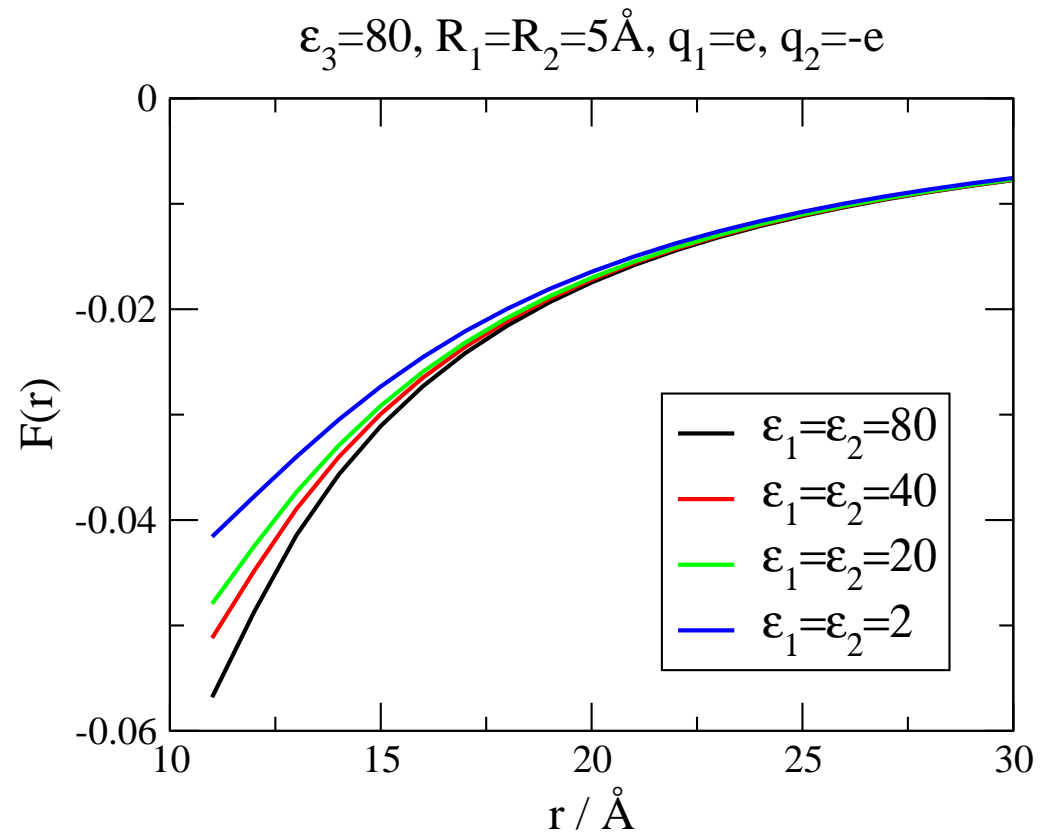
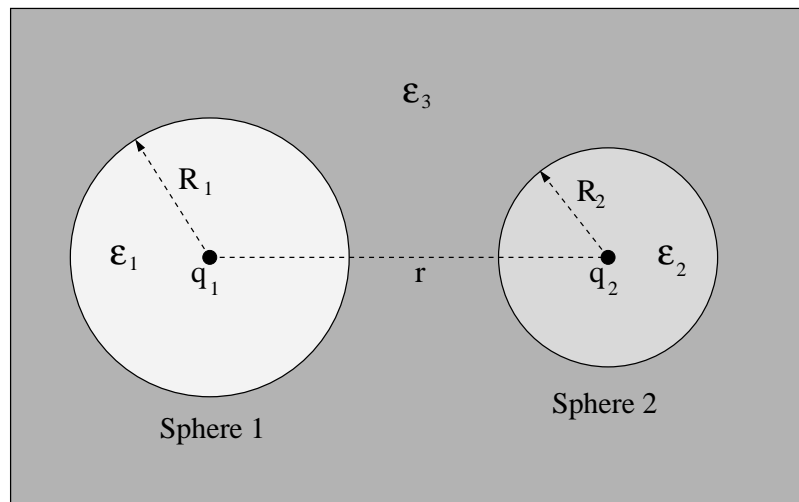
Source charge - induced charge energy as a function of the distance from the center of the sphere along the line on the charge and the sphere center

- 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

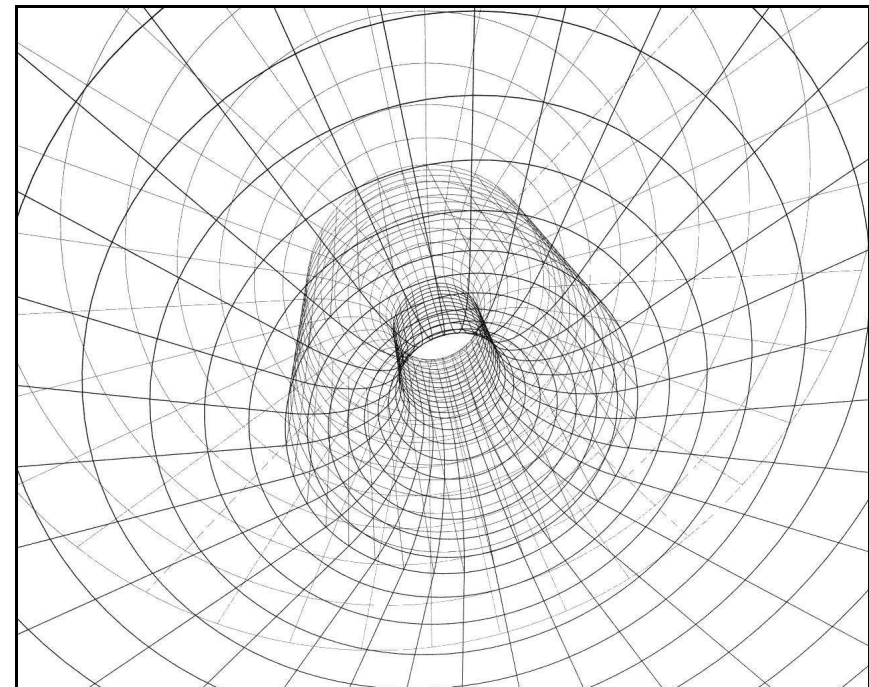
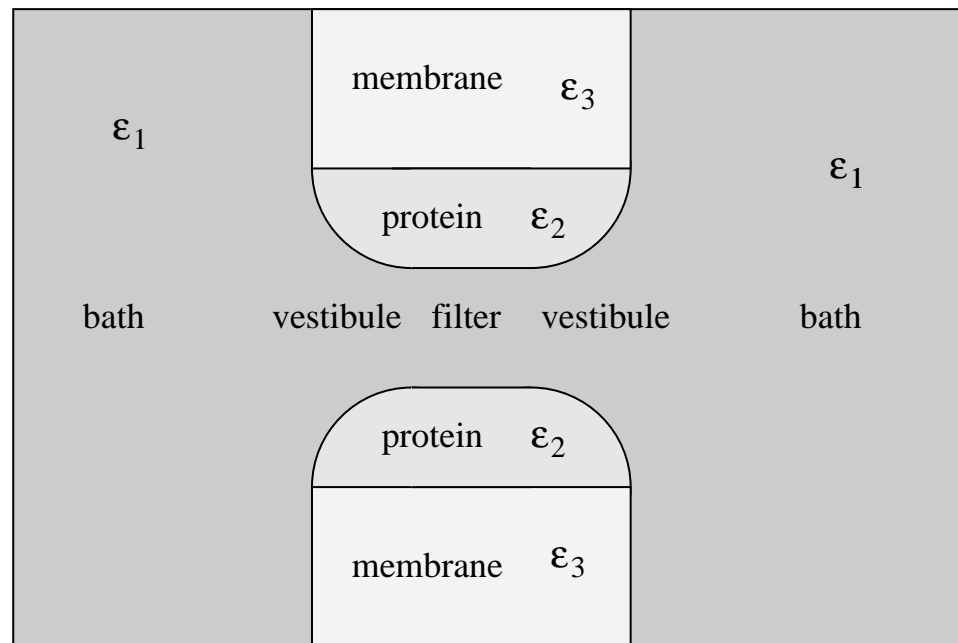
The effective pair potential is defined as $\varphi(r) = W(r) - W(r \rightarrow \infty)$. The energy $W(r \rightarrow \infty)$ corresponds to the interaction energy between the charge and the induced charge on its own sphere. The effective force is $F(r) = -d\varphi(r)/dr$.

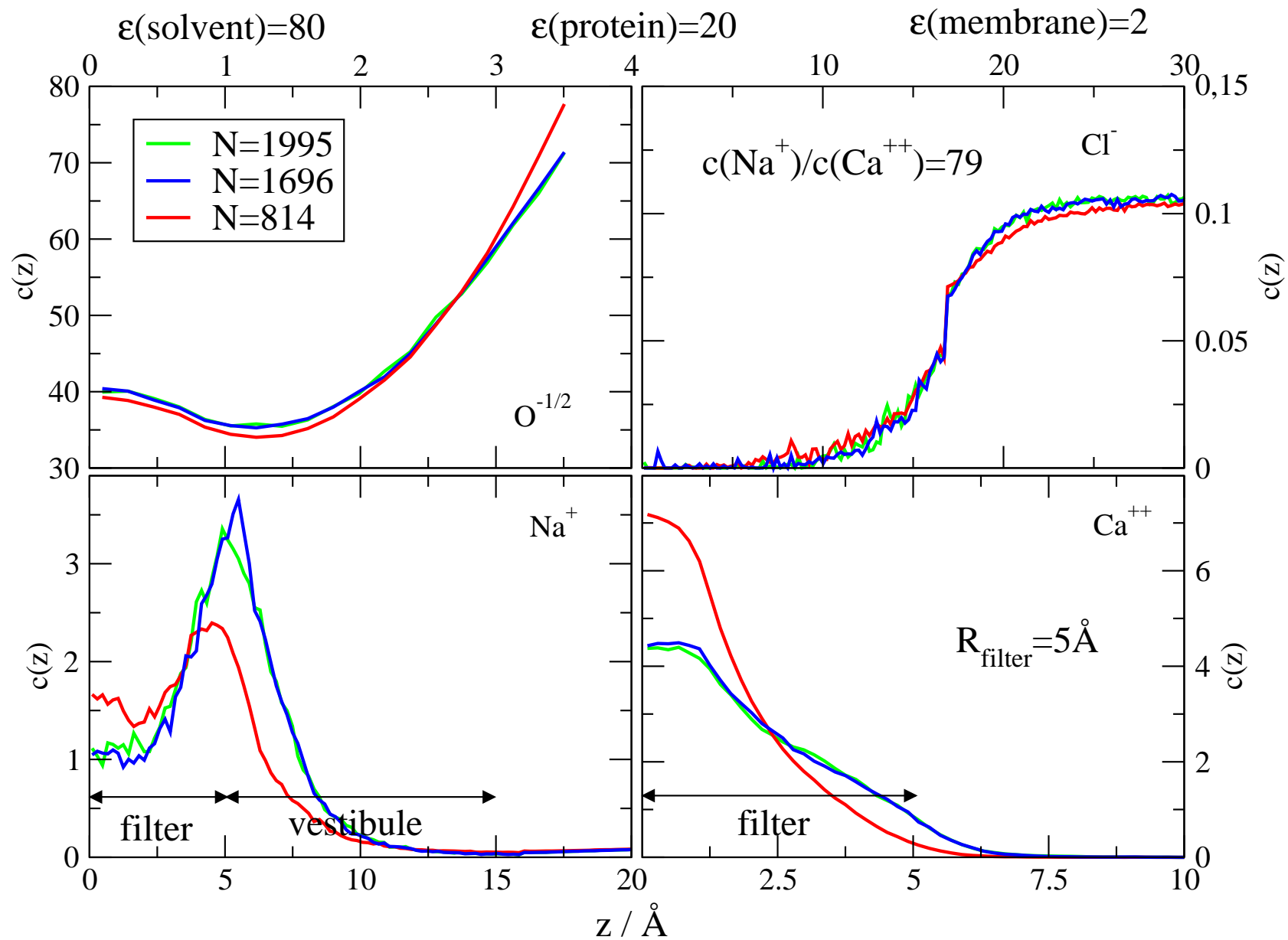


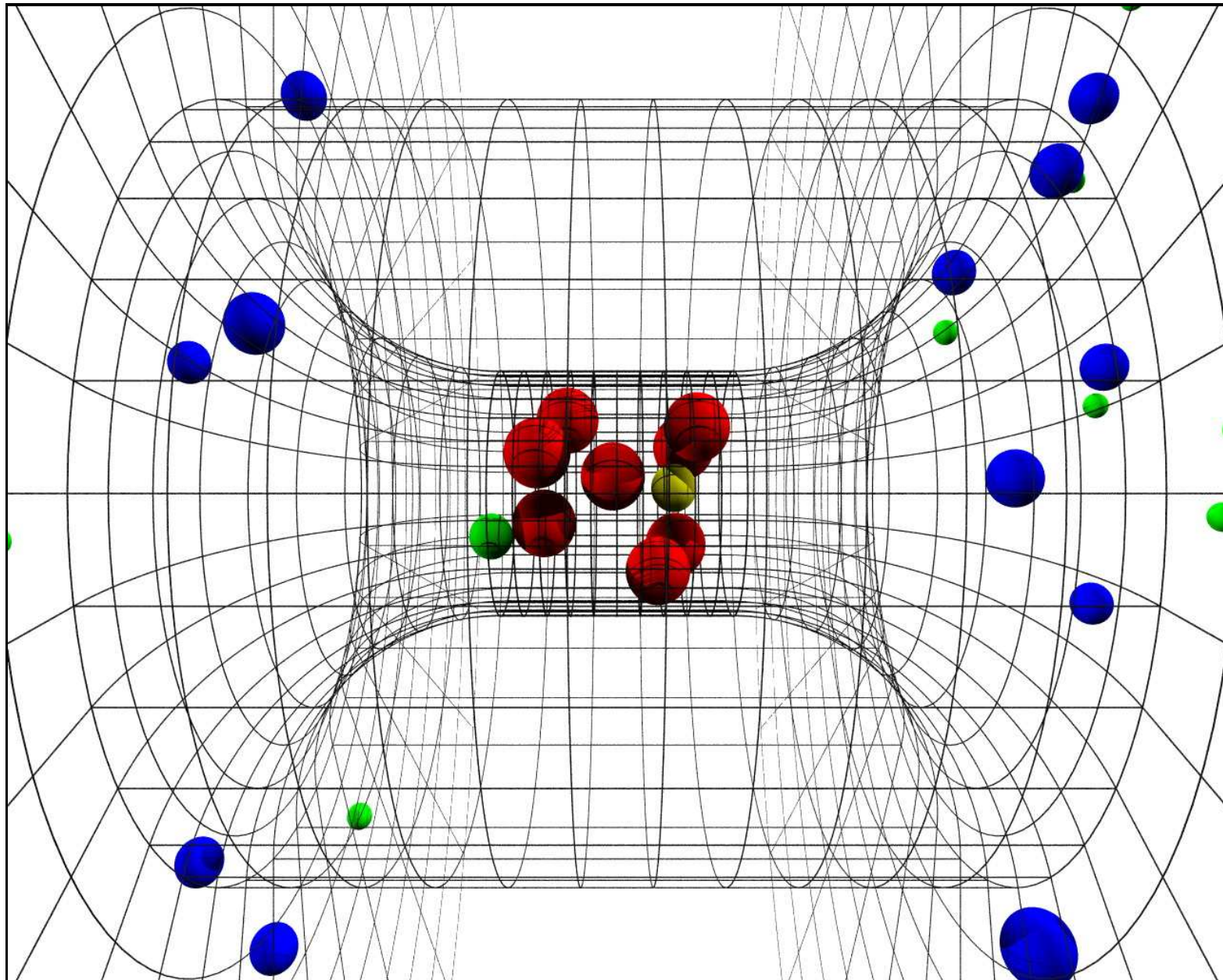
MC simulation for a model calcium channel

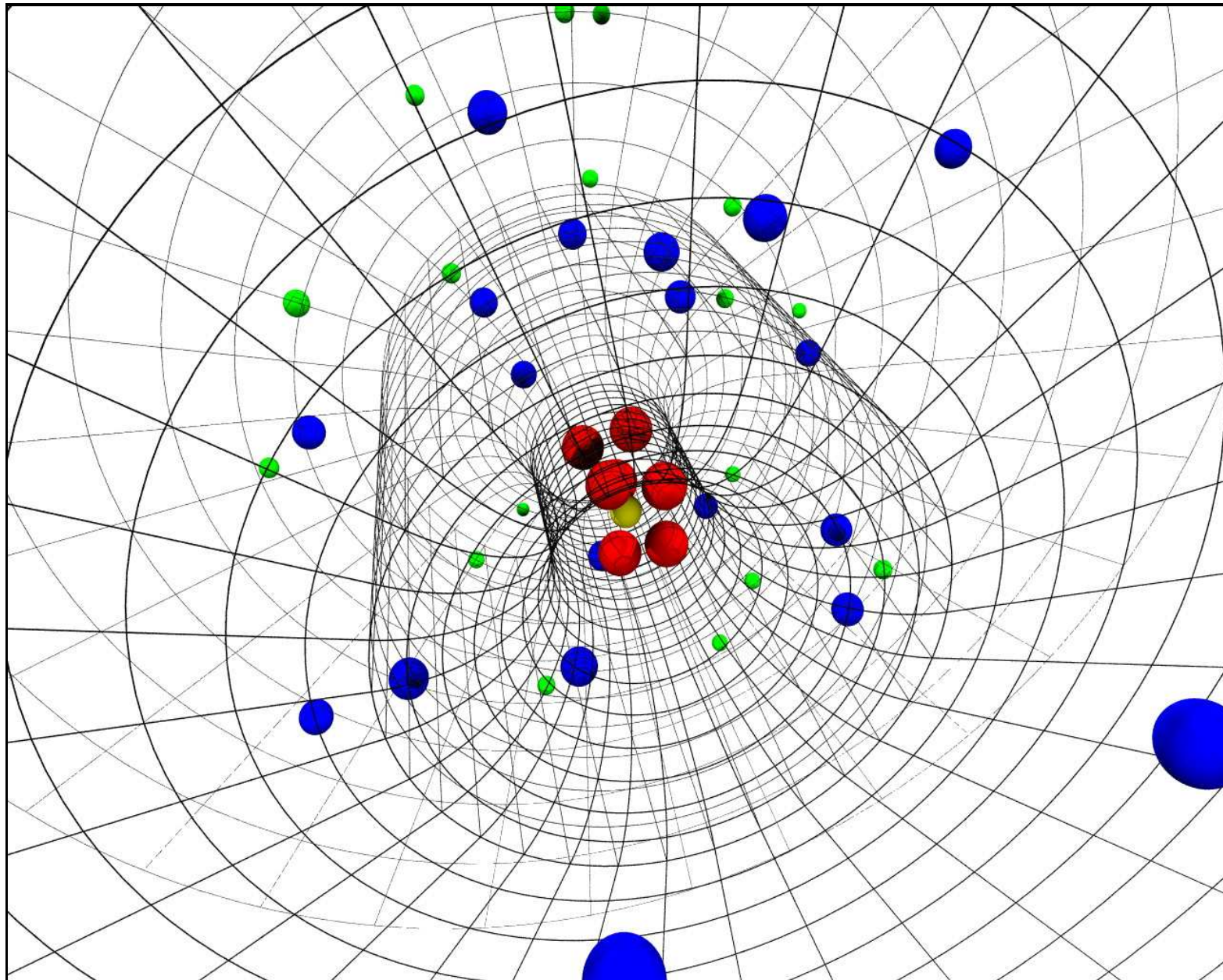
The selectivity filter of the calcium channel is known to be lined by 4 glutamate groups (EEEE locus). They are represented by 8 half charged oxygen ions that are confined to the filter but can move freely inside. A 0.1M NaCl solution used and a few Ca^{++} ions.

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









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