The Impact of Solvers on Modeling: The Solvation-Layer Interface Condition

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Collaborators

BEM and SLIC Collaboration

Jay Bardhan

Main Question

How do available solvers influence our choice of model?

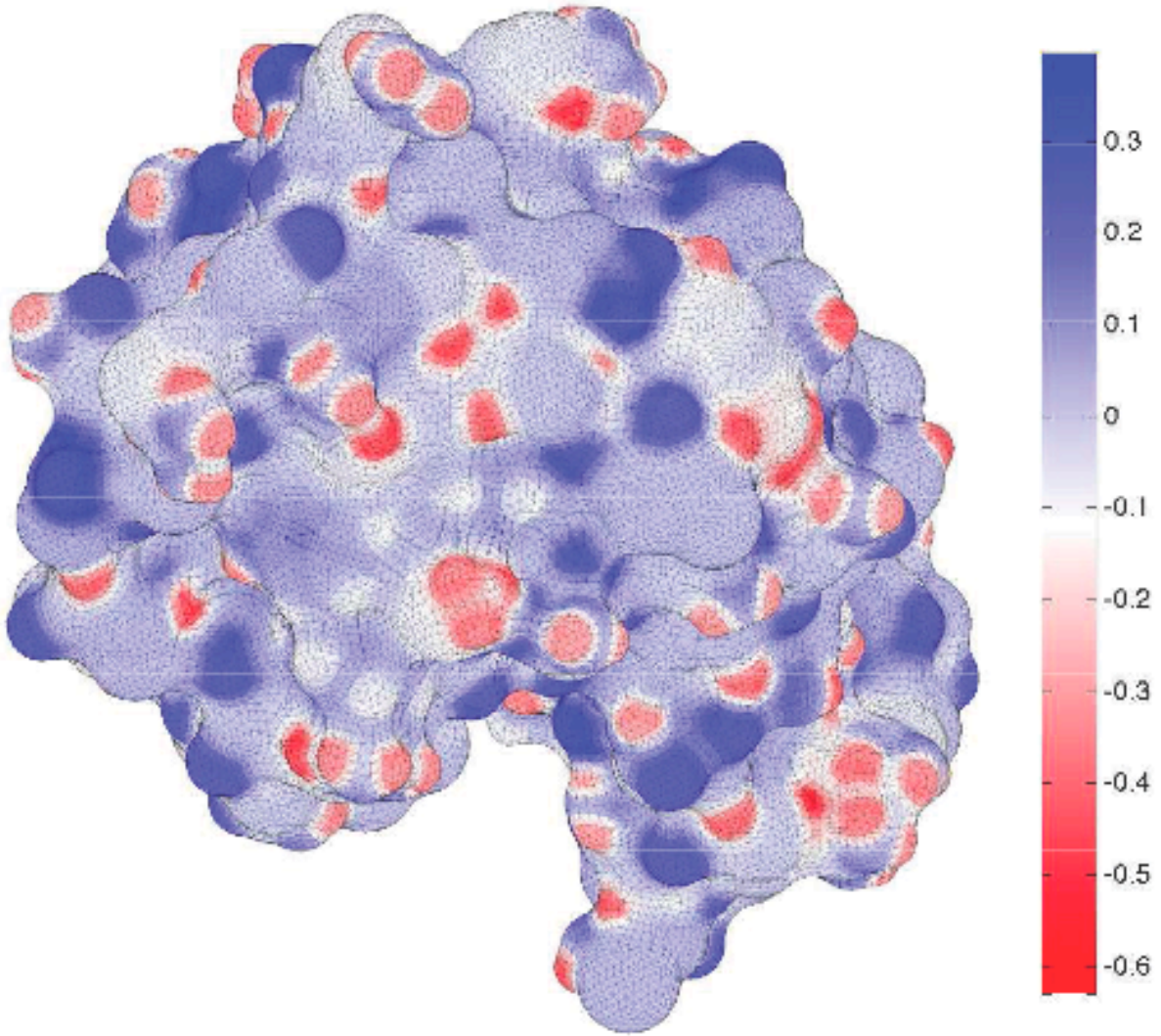
Nonlinear BEM

Nonlinear BEM is powerful,
but neglected because
it requires specialized solvers.

Outline

Bioelectrostatics

The Natural World

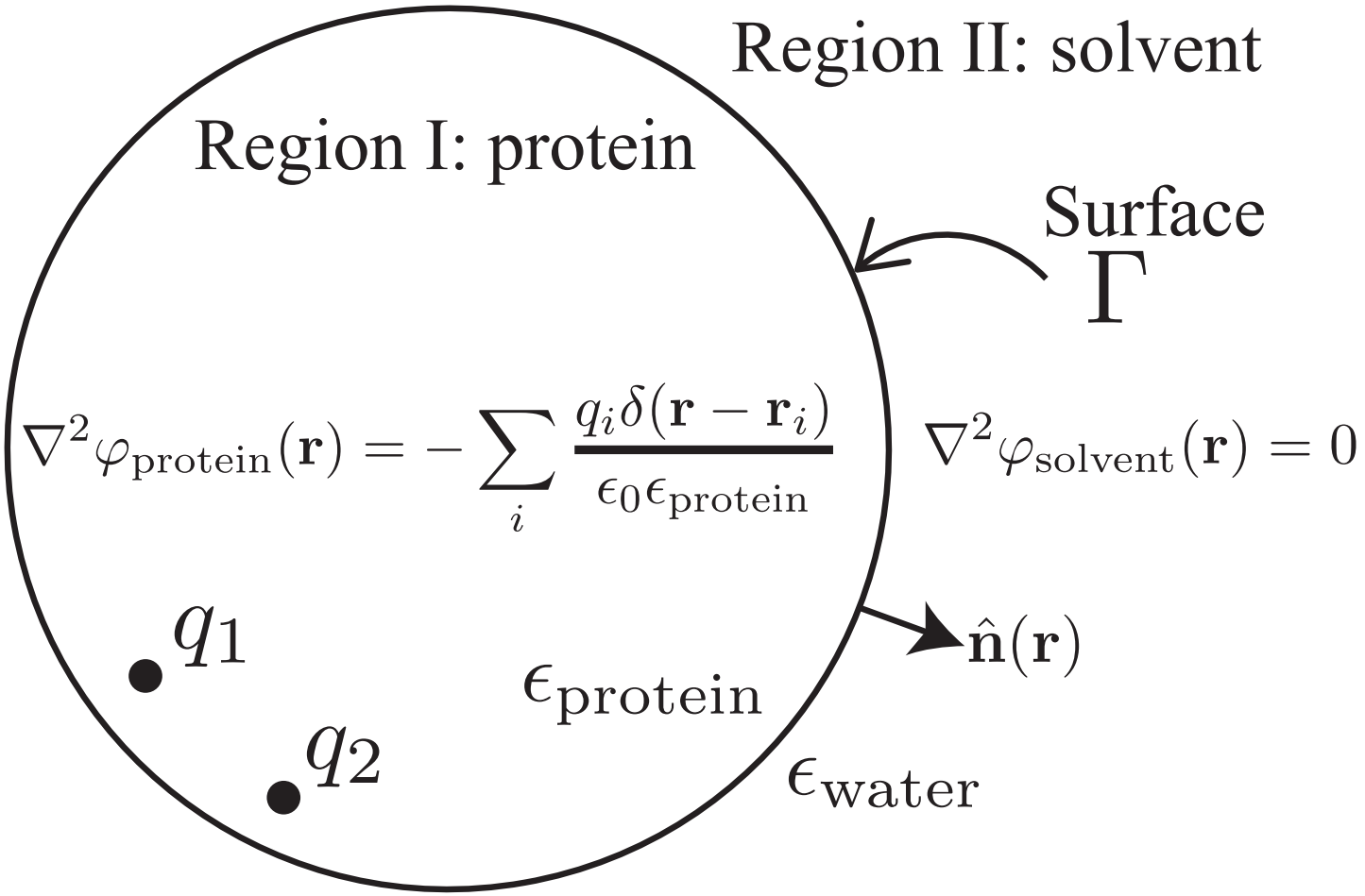


Induced Surface Charge on Lysozyme

Bioelectrostatics

Physical Model

Electrostatic Potential ϕ



Bioelectrostatics

Mathematical Model

We can write a Boundary Integral Equation (BIE) for the induced surface charge σ,

$$\sigma(\vec{r}) + \hat{\epsilon} \int_\Gamma \frac{\partial}{\partial n(\vec{r})} \frac{\sigma(\vec{r}')d^2\vec{r}'}{4\pi||\vec{r} - \vec{r}'||} = -\hat{\epsilon} \sum_{k=1}^{Q} \frac{\partial}{\partial n(\vec{r})} \frac{q_k}{4\pi||\vec{r} - \vec{r}_k||}$$

$$\left(\mathcal{I} + \hat{\epsilon}\mathcal{D}^*\right)\sigma(\vec{r}) =$$

where we define

$$\hat{\epsilon} = 2\frac{\epsilon_I - \epsilon_{II}}{\epsilon_I + \epsilon_{II}} < 0$$

Biomolecular Modeling

Problems

This model is inaccurate for solvation energy.

Biomolecular Modeling

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This model is inaccurate for solvation energy.

Thus practitioners adjust atomic radii to fit full atomistic simulation energies.

Biomolecular Modeling

Problems

However, a given atom

- can have two different radii in different molecules

Biomolecular Modeling

Problems

However, a given atom

- can have two different radii in different molecules
- can have two different radii in the same molecule

Biomolecular Modeling

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However, a given atom

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- has a solvent-dependent radius

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- has a temperature-dependent radius

Biomolecular Modeling

Problems

However, a given atom

- can have two different radii in different molecules
- can have two different radii in the same molecule
- has a solvent-dependent radius
- has a temperature-dependent radius

For example, the volume of a carbon atom can vary by 50% in a single molecule.

Biomolecular Modeling

Problems

Why is this a bad model?

- Ignores experimental data (crystal radii)

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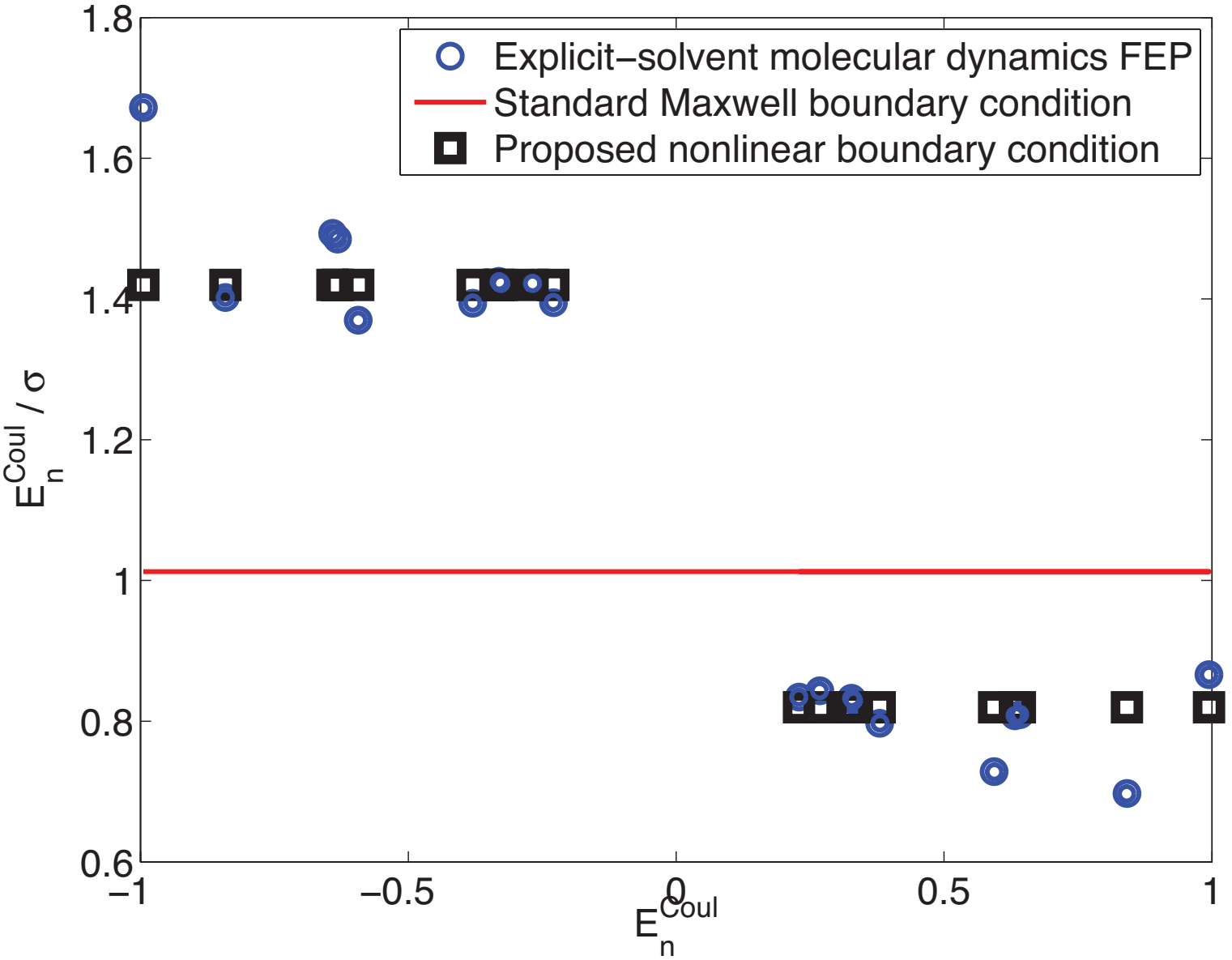
Biomolecular Modeling

Problems

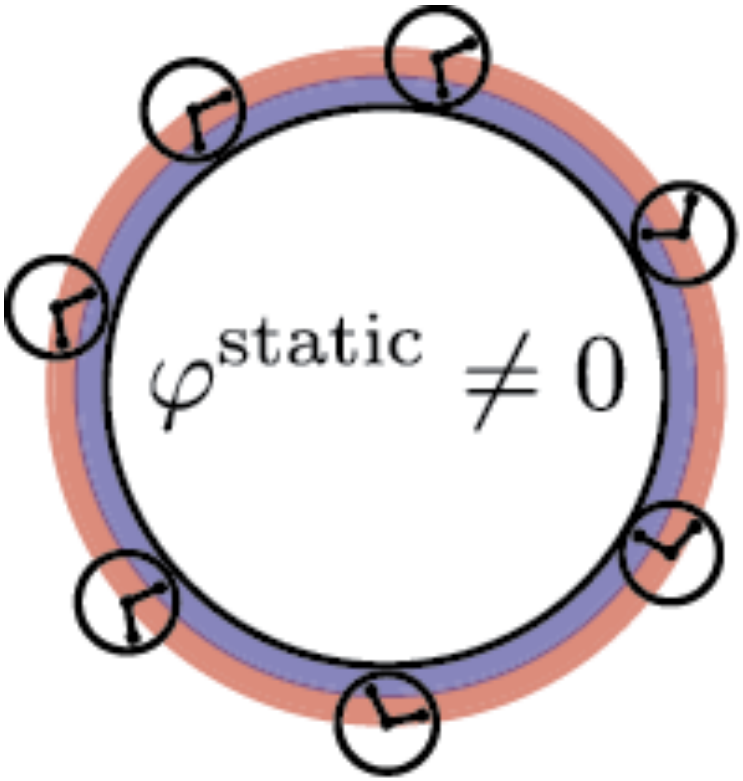
Why is this a bad model?

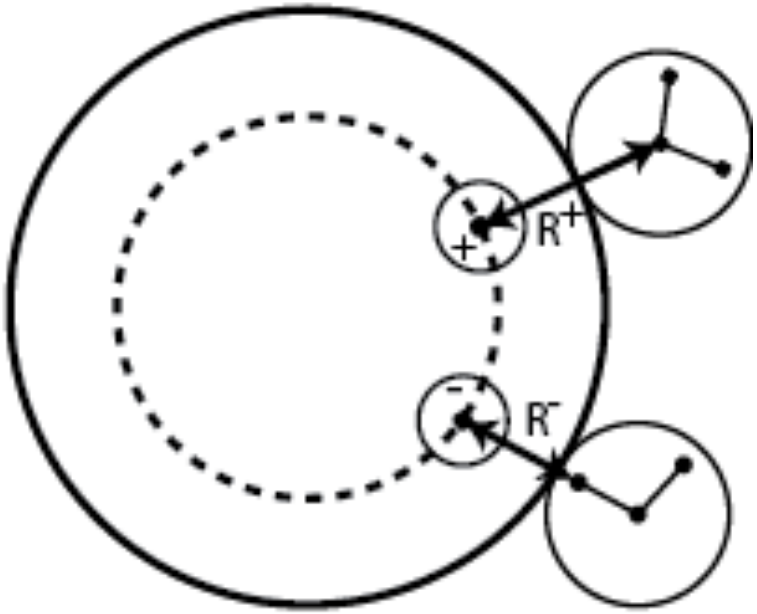
- Ignores experimental data (crystal radii)
- Not robust to solute/solvent/temperature changes
- Misses sensitivity to local electrostatic conditions
- Gives nonsense for the entropy

Origins of Electrostatic Asymmetry

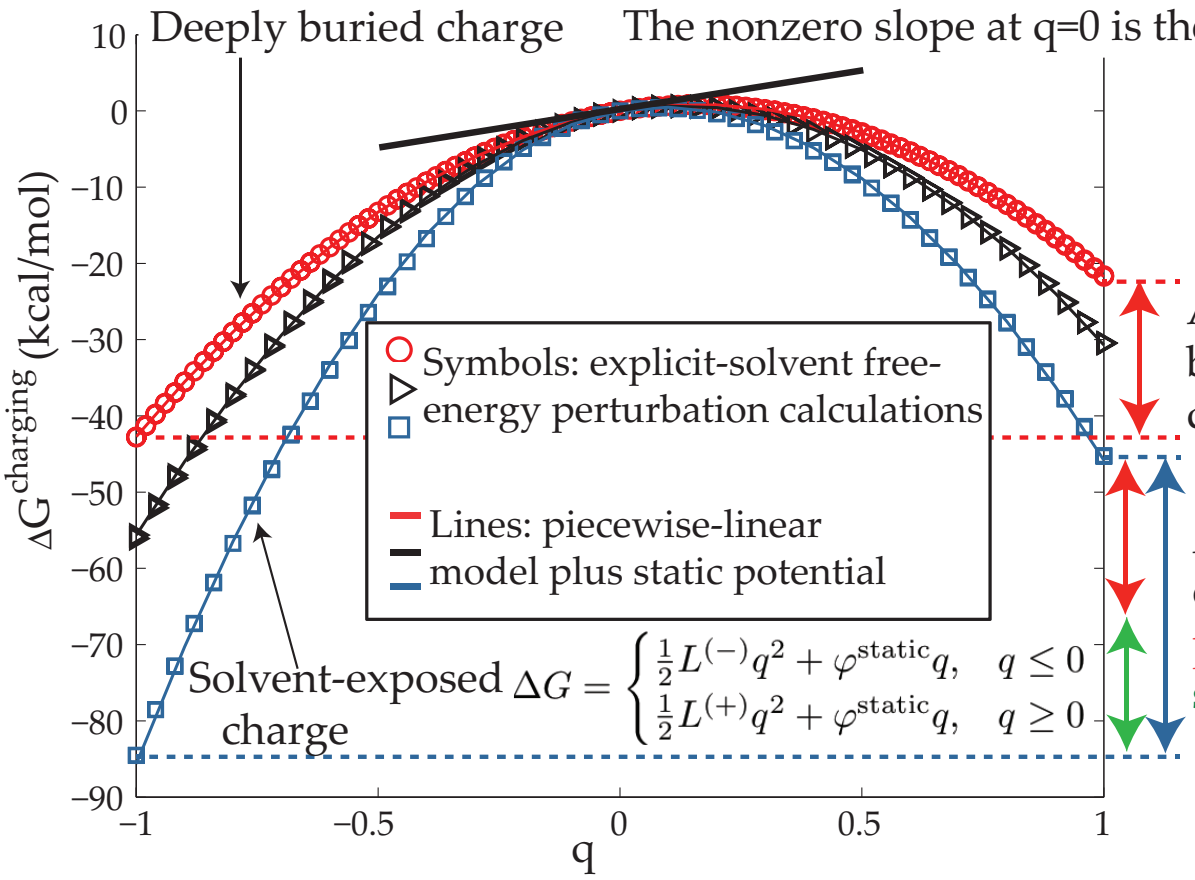


Origins of Electrostatic Asymmetry





Origins of Electrostatic Asymmetry



Asymmetry for a deeply buried charge is exclusively due to the static potential

Asymmetry for a solvent-exposed charge results from both the static potential and the hydrogen-oxygen size difference

Main Idea

Solvation-Layer Interface Condition (SLIC)

Instead of assuming the model and energy and deriving the radii,

$$\epsilon_I \frac{\partial \Phi_I}{\partial n} = \epsilon_{II} \frac{\partial \Phi_{II}}{\partial n}$$

Main Idea

Solvation-Layer Interface Condition (SLIC)

assume the energy and radii and derive the model.

$$(\epsilon_I - \Delta\epsilon h(E_n)) \frac{\partial \Phi_I}{\partial n} = (\epsilon_{II} - \Delta\epsilon h(E_n)) \frac{\partial \Phi_{II}}{\partial n}$$

Main Idea

Solvation-Layer Interface Condition (SLIC)

Using our correspondence with the BIE form,

$$\left(\mathcal{I} + h(E_n) + \hat{\epsilon}\left(-\frac{1}{2}\mathcal{I} + \mathcal{D}^*\right)\right)\sigma = \hat{\epsilon}\sum_{k=1}^{Q}\frac{\partial G}{\partial n}$$

where h is a diagonal nonlinear integral operator.

SLIC

Boundary Perturbation

$$h(E_n) = \alpha \tanh\left(\beta E_n - \gamma\right) + \mu$$

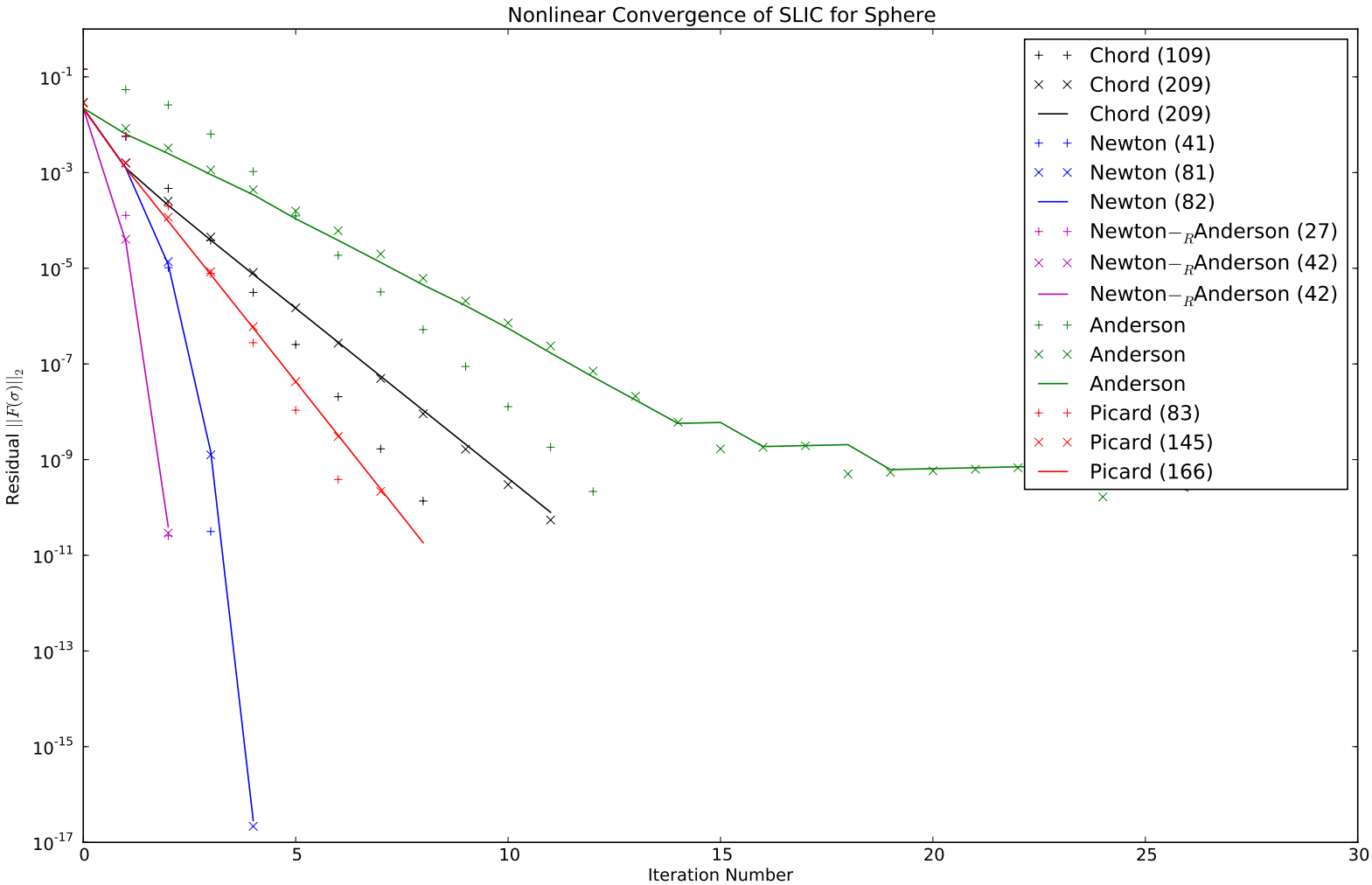
where

- α Size of the asymmetry
- β Width of the transition region
- γ The transition field strength
- μ Assures $h(0) = 0$, so $\mu = -\alpha \tanh(-\gamma)$

Outline

Solving SLIC

Sphere



Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Richardson's Method

$$u_{n+1} = u_n + \lambda \left(F(u_n) - b \right)$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Richardson's Method

```
-snes_type nrichardson
-snes_linesearch_type l2
-snes_linesearch_damping 0.05
```

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton's Method

$$u_{n+1} = u_n + J^{-1}(u_n)\left(F(u_n) - b\right)$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton's Method

```
-snes_type newtonls
-snes_linesearch_type basic
```

Nonlinear Solvers

If we are solving

$$Au + N(u)u = b$$

with Picard's Method

$$\left(A + \mathrm{diag}(h(u_n))\right) u_{n+1} = b$$

Nonlinear Solvers

If we are solving

$$Au + \mathrm{diag}(h(u))u = b$$

with Picard's Method

$$(A + \mathrm{diag}(h(u_n)))\, u_{n+1} = b$$

Nonlinear Solvers

If we are solving

$$Au + \mathrm{diag}(h(u))u = b$$

with Picard's Method

$$J = A + \mathrm{diag}(h(u_n)) + \mathrm{diag}(h'(u_n))K'$$
$$J_P = A + \mathrm{diag}(h(u_n))$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Generalized Broyden Method

$$u_{n+1} = u_n + \beta\left(F(u_n) - b\right) - \left(\mathbb{X}_k + \beta F(u_k)\right)\gamma_k$$
$$\gamma_i = \left(\mathcal{F}^T(u_k)\mathcal{F}(u_k)\right)^{-1}\mathcal{F}^T(u_i)\left(F(u_i) - b\right)$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Generalized Broyden Method

```
-snes_type ngmres
-snes_linesearch_type l2
```

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton $-_R$ Generalized Broyden Method

$$y = \mathcal{N}(F(\mathcal{GB}(F, \cdot, b)), x_n, b)$$
$$x_{n+1} = \mathcal{GB}(F, y, b)$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton $-_R$ Generalized Broyden Method

$$u' = \mathcal{GB}(F, u_n, b)$$
$$u_{n+1} = u' + J^{-1}(u')\left(F(u') - b\right)$$

Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton $-_R$ Generalized Broyden Method

```
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-snes_linesearch_type basic
-npc_snes_type ngmres
-npc_snes_max_it 2
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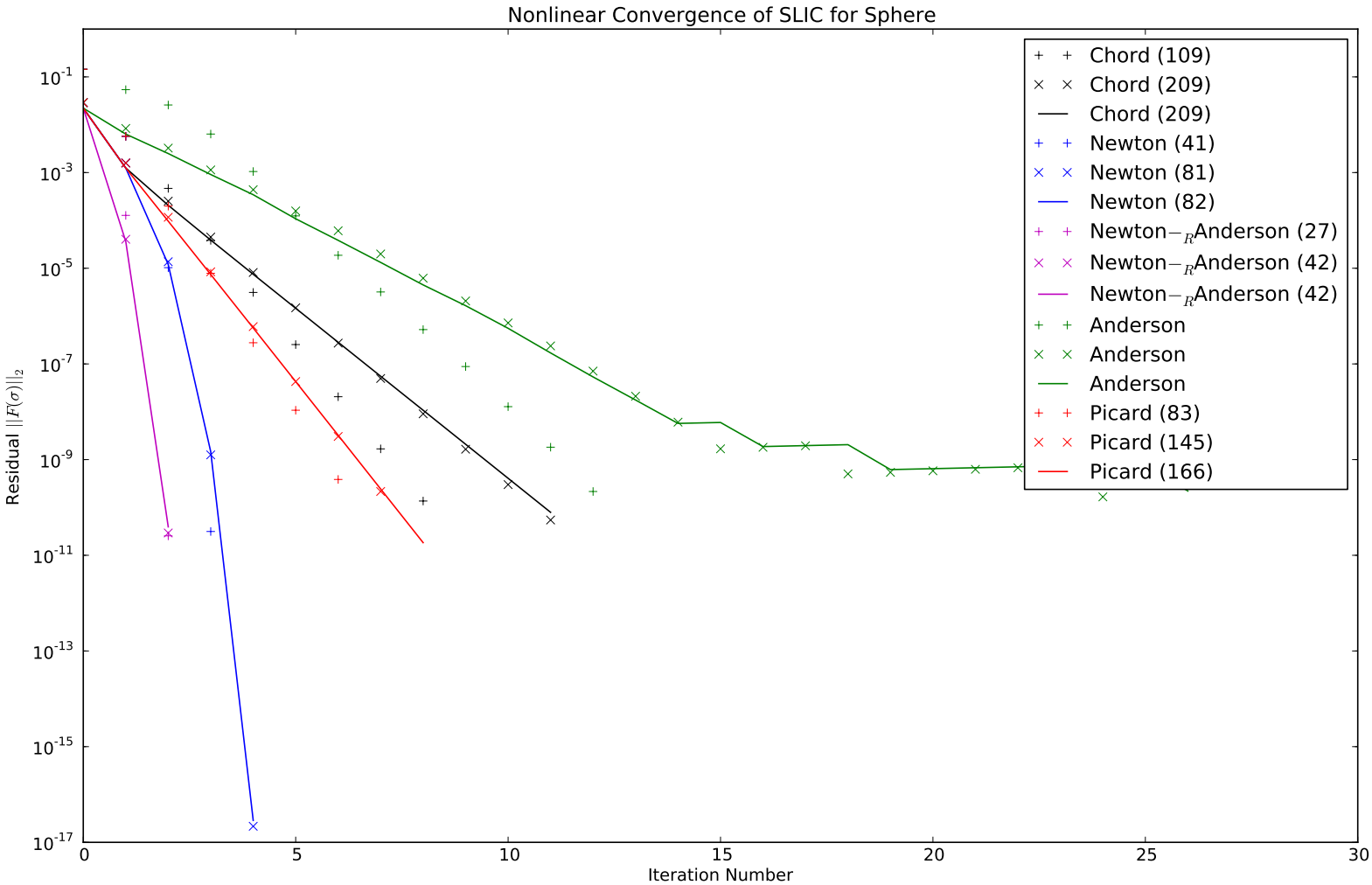
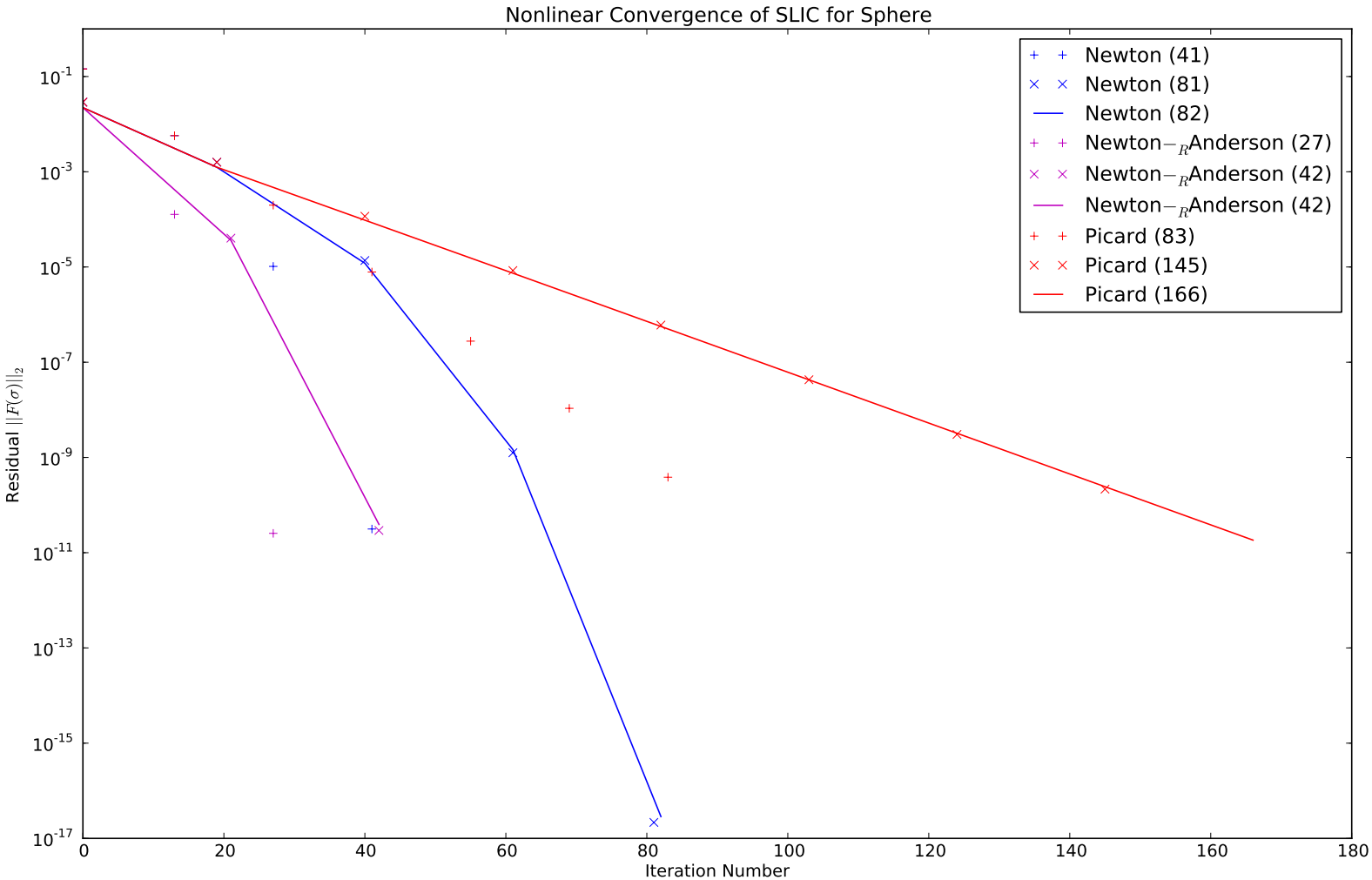
Solving SLIC

Sphere

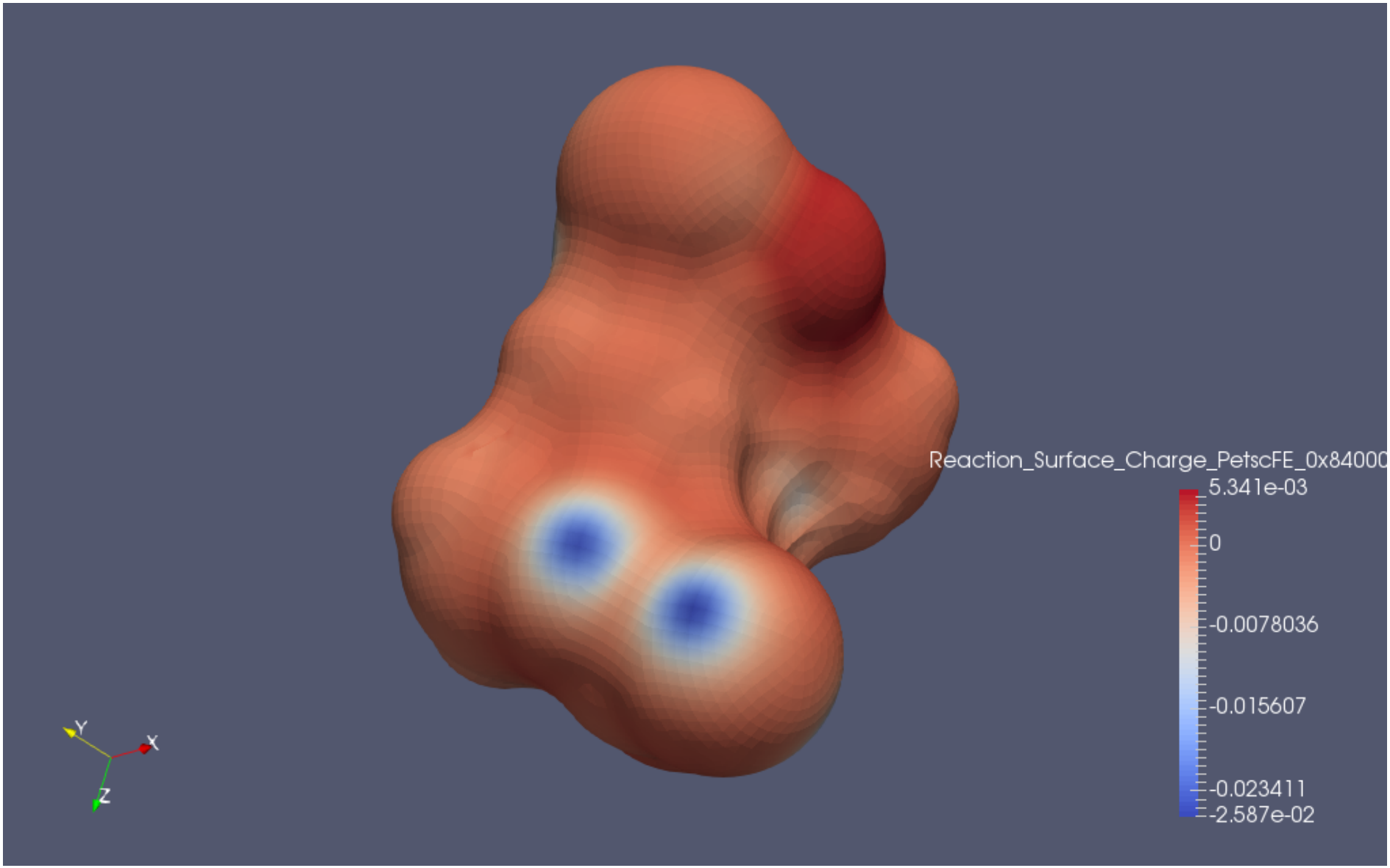


Solving SLIC

Sphere

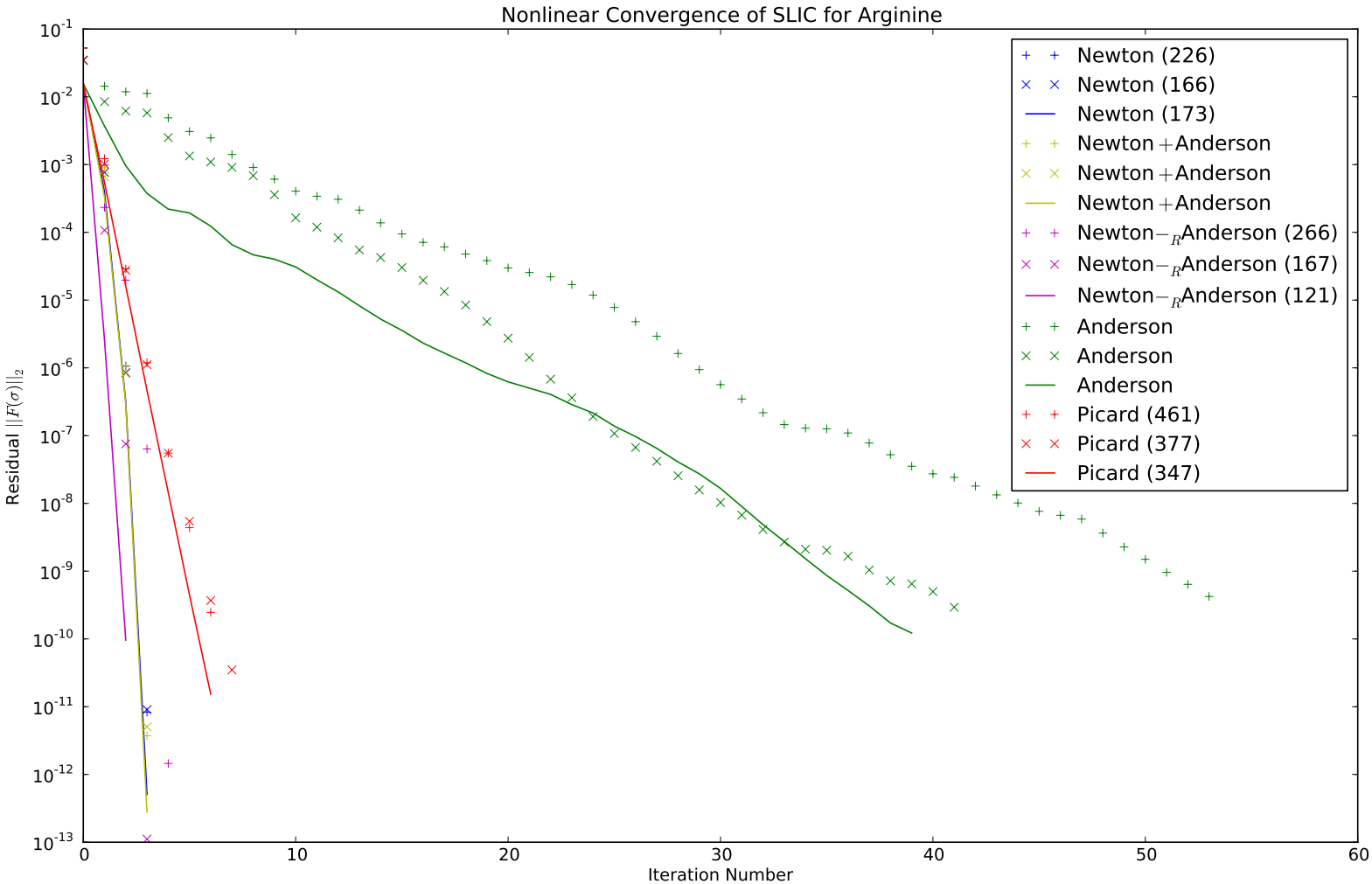


ARG


Reaction_Surface_Charge_PetscFE_0x84000
5.341e-03
0
-0.0078036
-0.015607
-0.023411
-2.587e-02
Y
X
Z

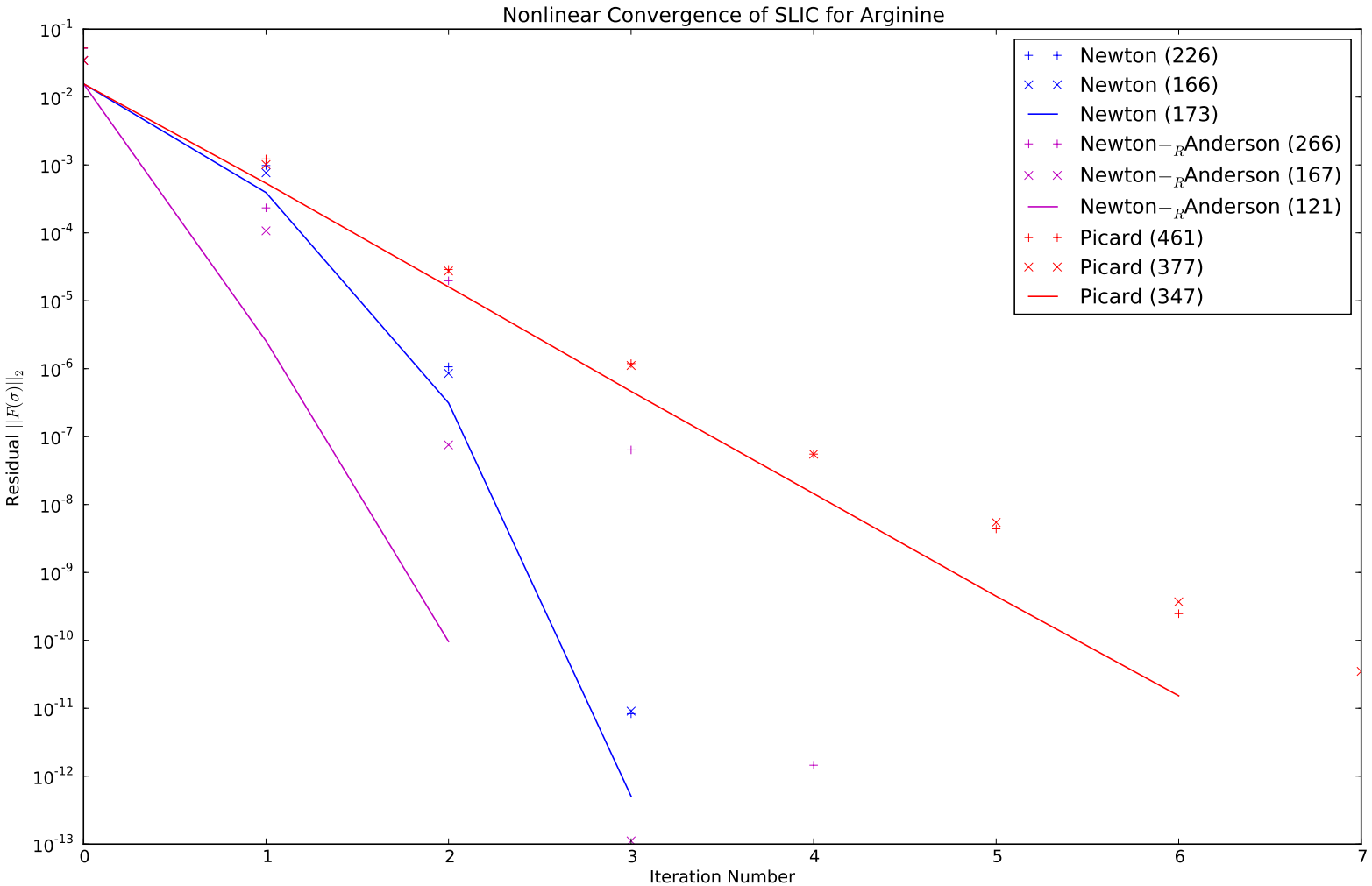
Solving SLIC

Arginine



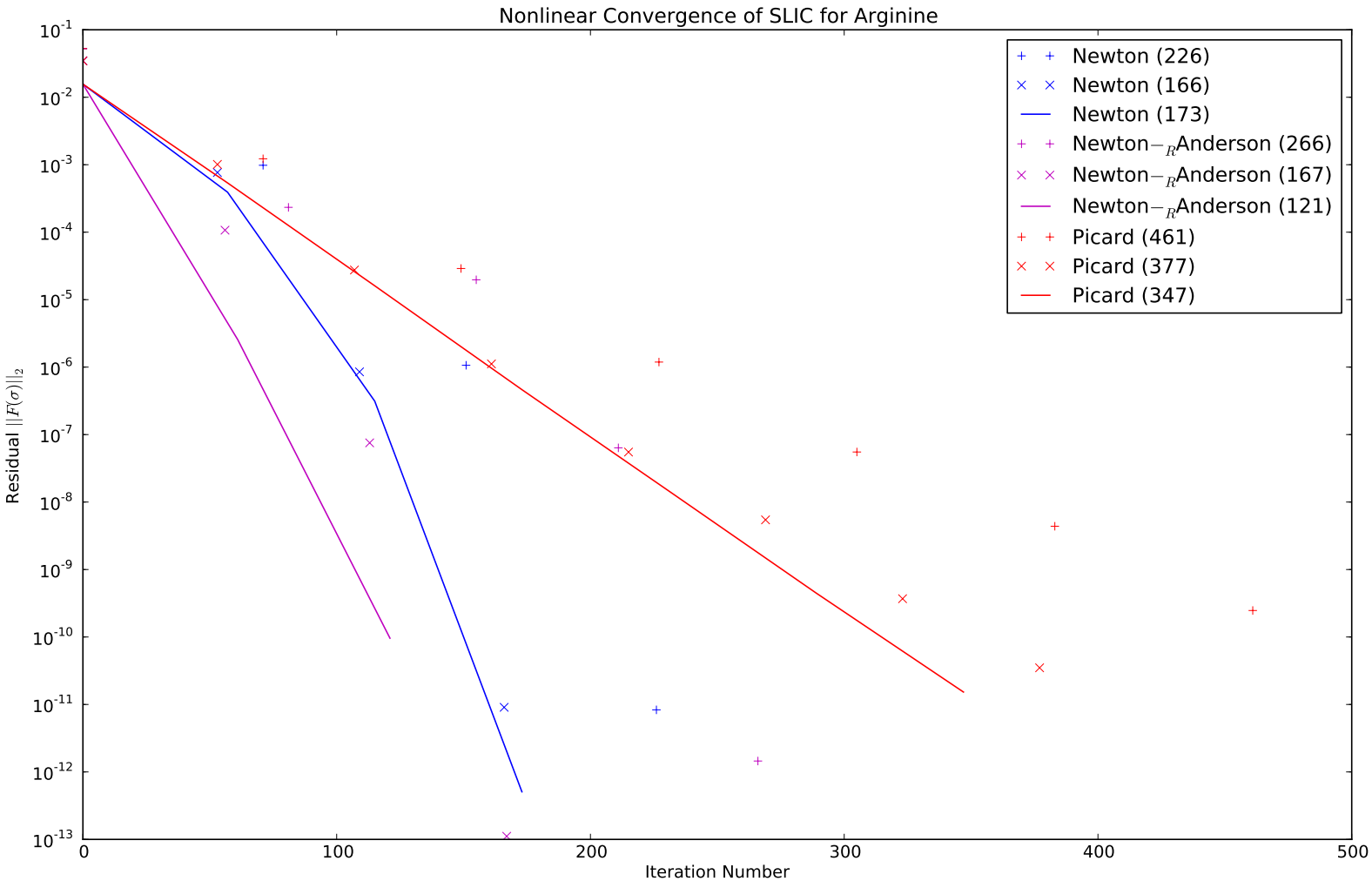
Solving SLIC

Arginine



Solving SLIC

Arginine



Outline

Main Conclusion

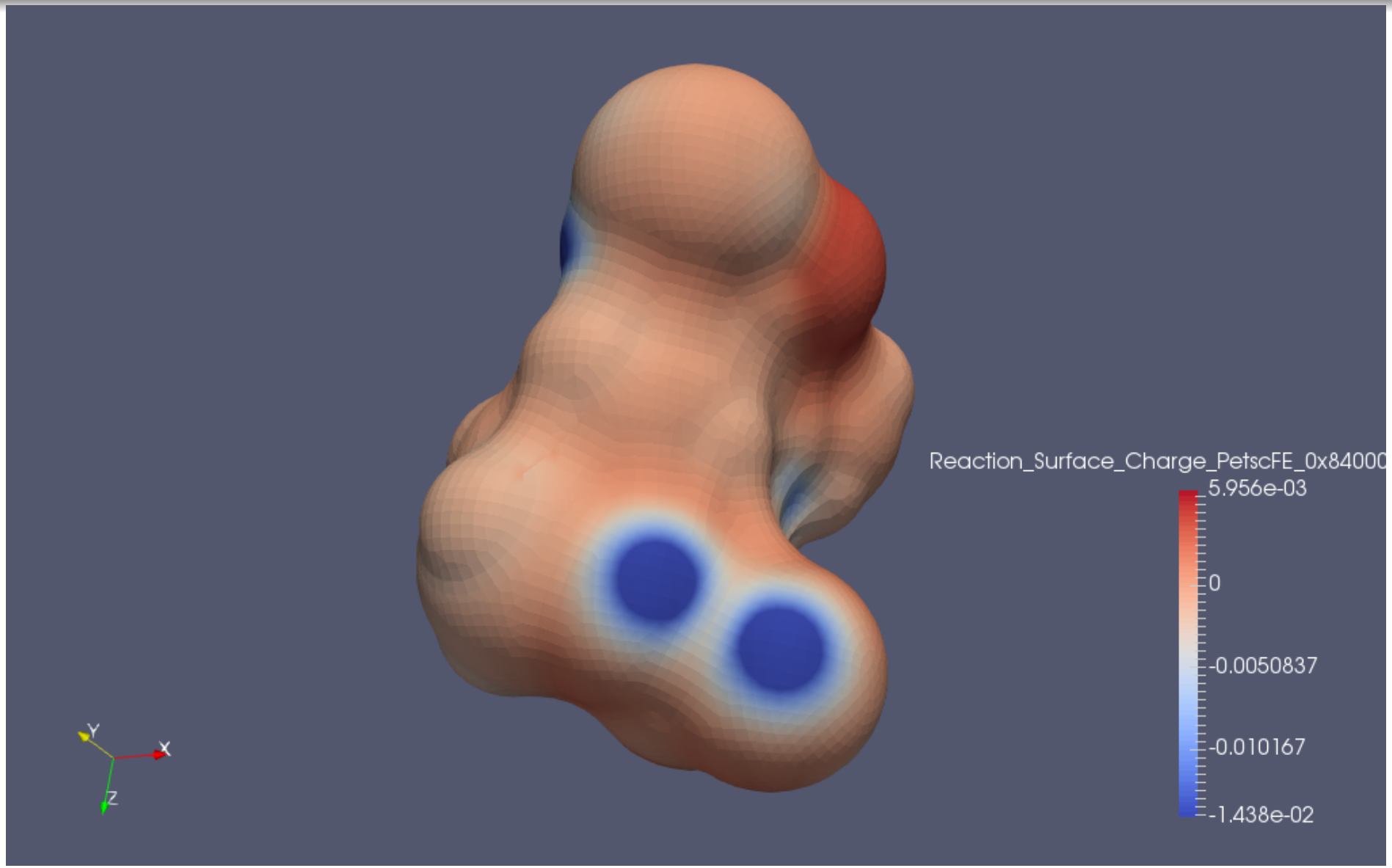
Nonlinear Preconditioning

can lead to significant speedups,

and is accessible without recoding.

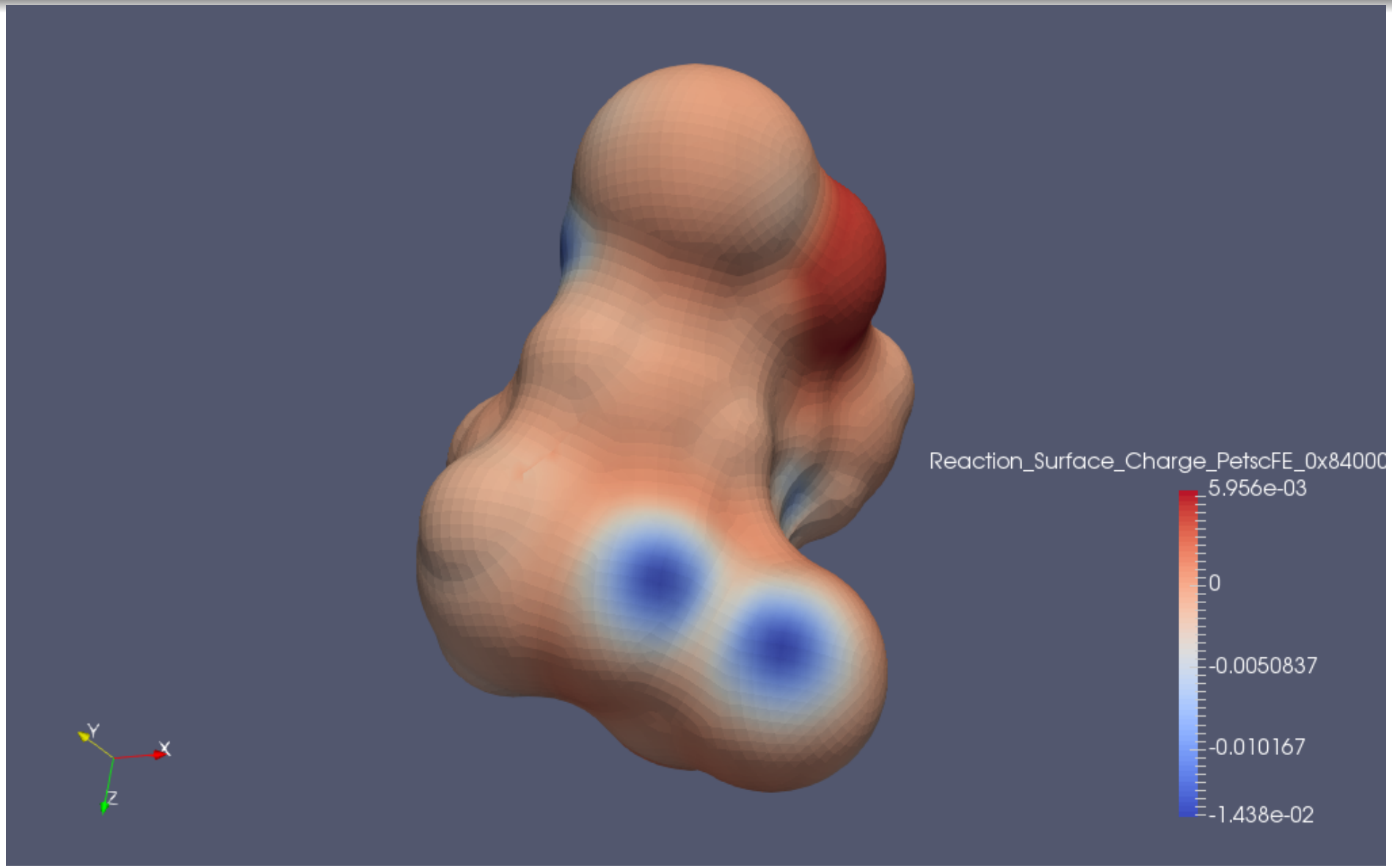
Charge Distribution

Maxwell



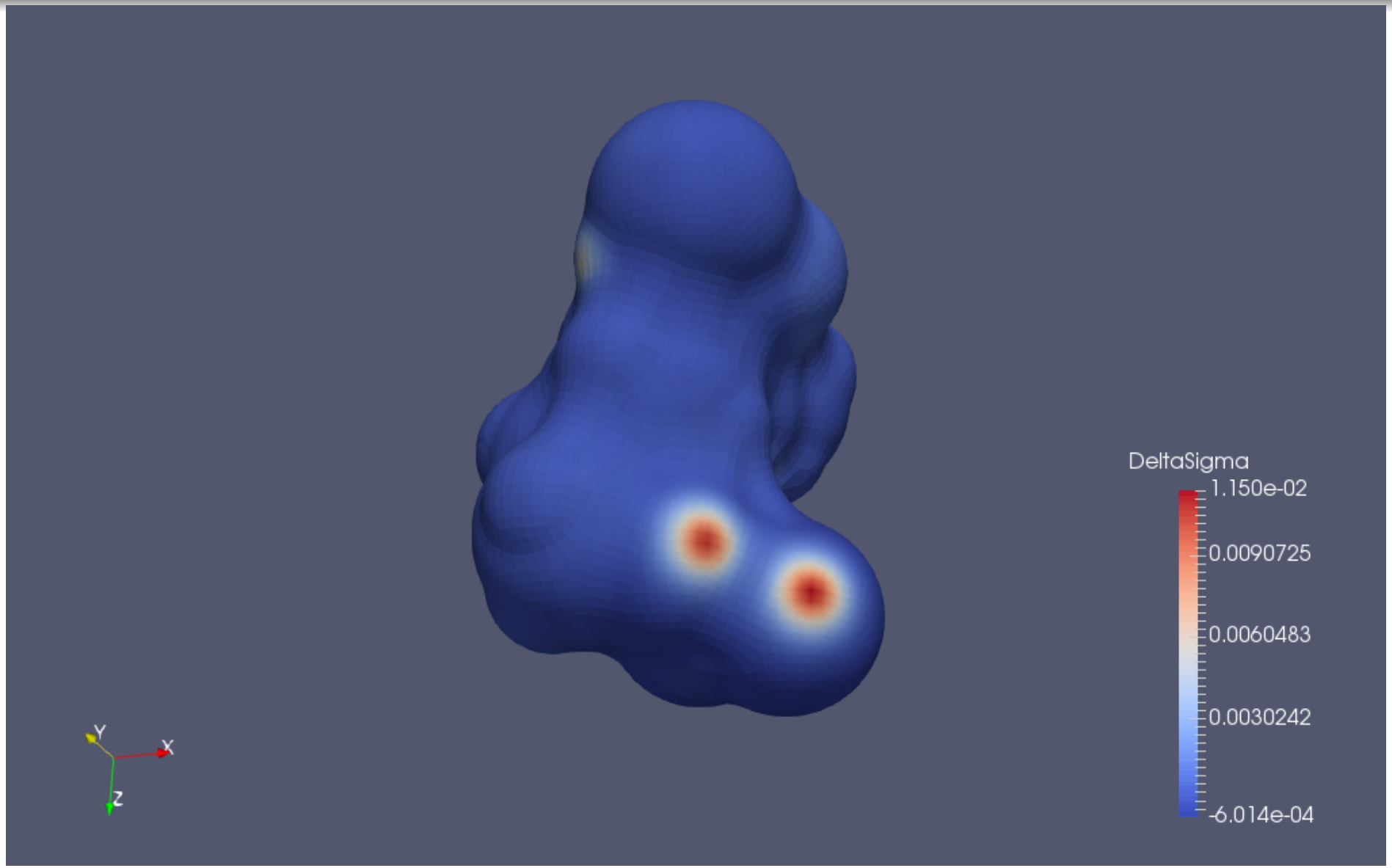
Charge Distribution

SLIC



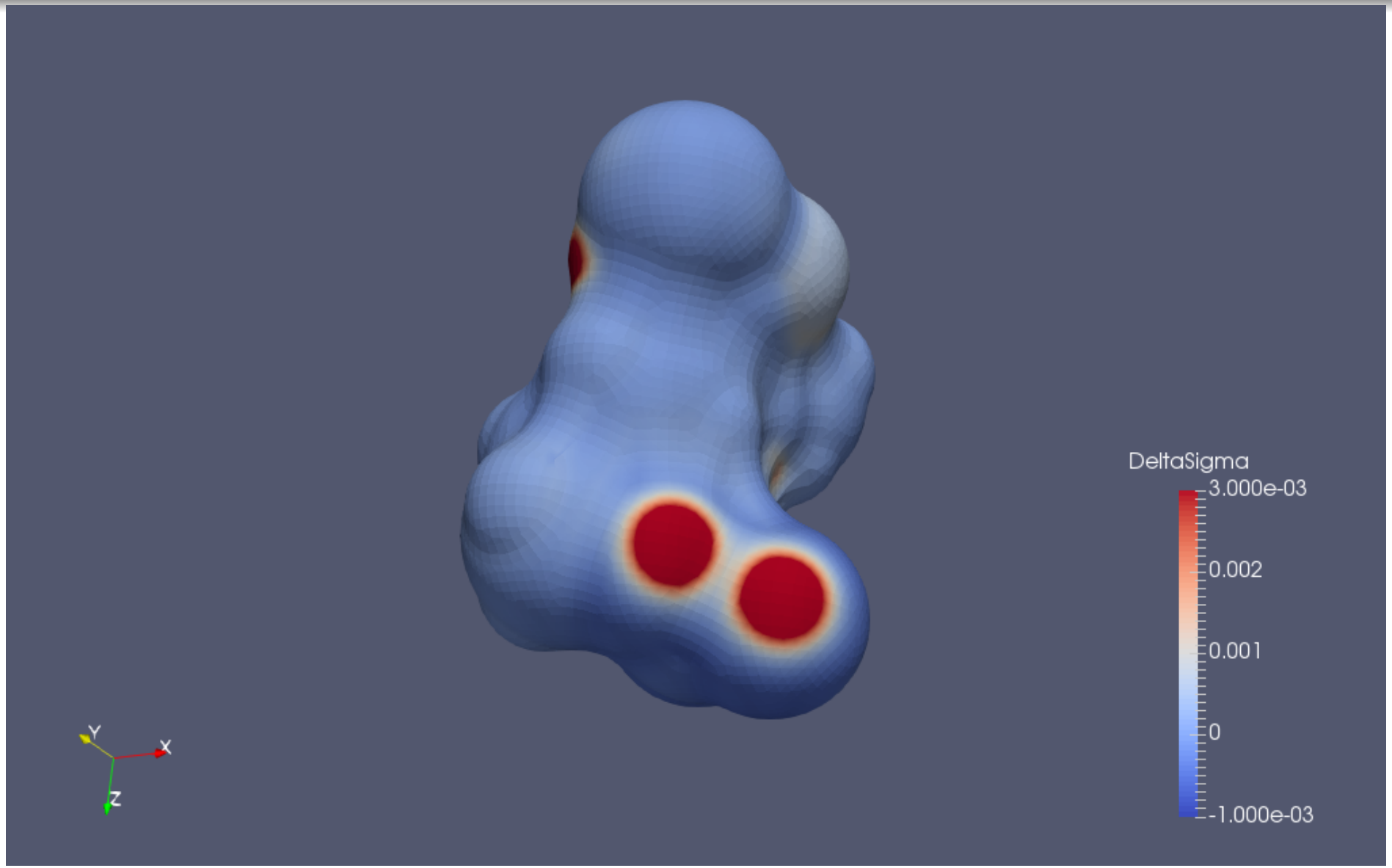
Charge Distribution

Difference



Charge Distribution

Difference (Rescaled)



Future Work

- Cathodic Protection/Corrosion Prevention
- Homogenized boundary conditions
- Models of the hydrophobic interaction

Thank You!

http://cse.buffalo.edu/~knepley