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

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# Collaborators

BEM and SLIC Collaboration

Jay Bardhan

# Main Question

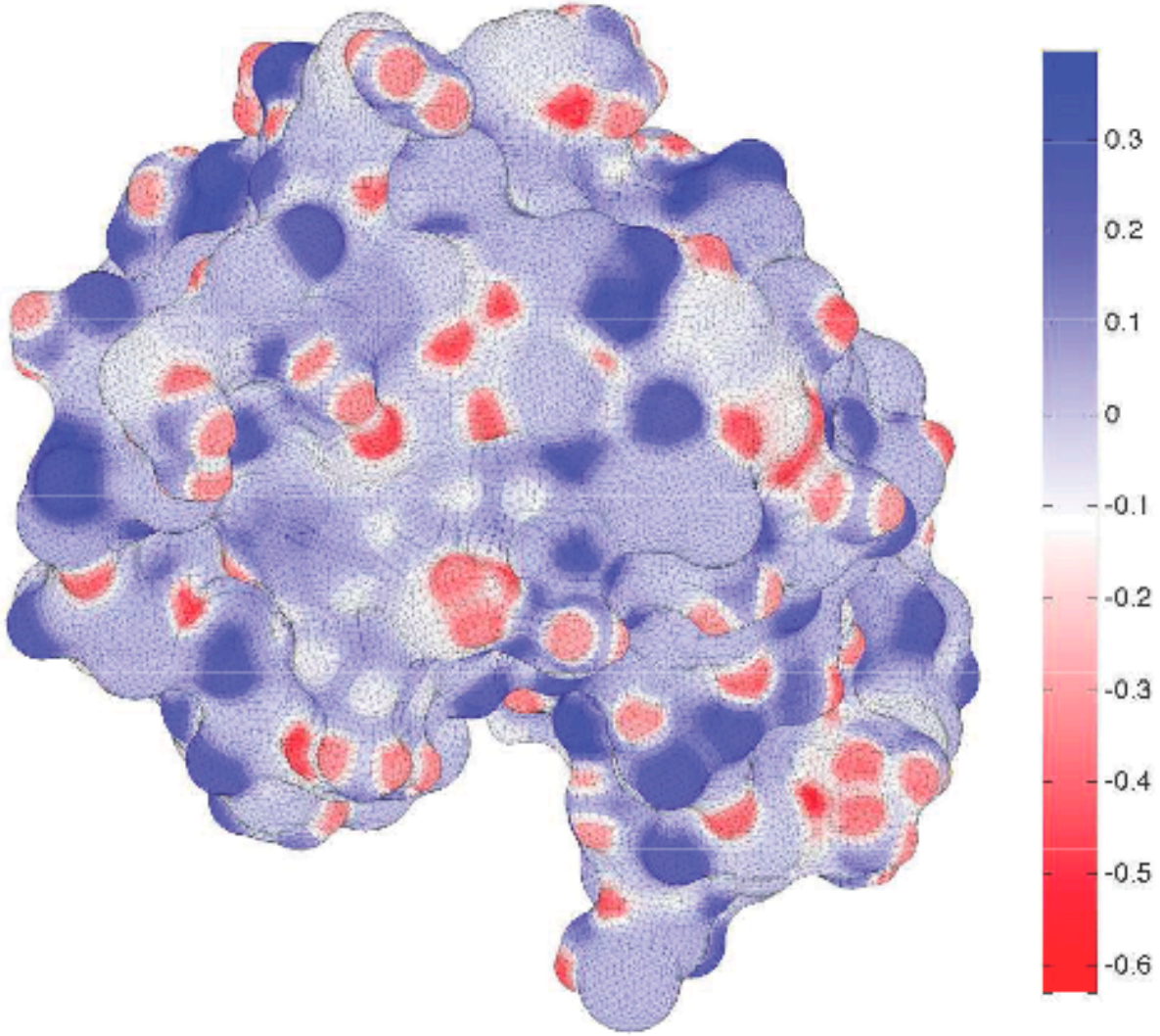
How do available solvers influence our choice of model?

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

# Outline

# Bioelectrostatics

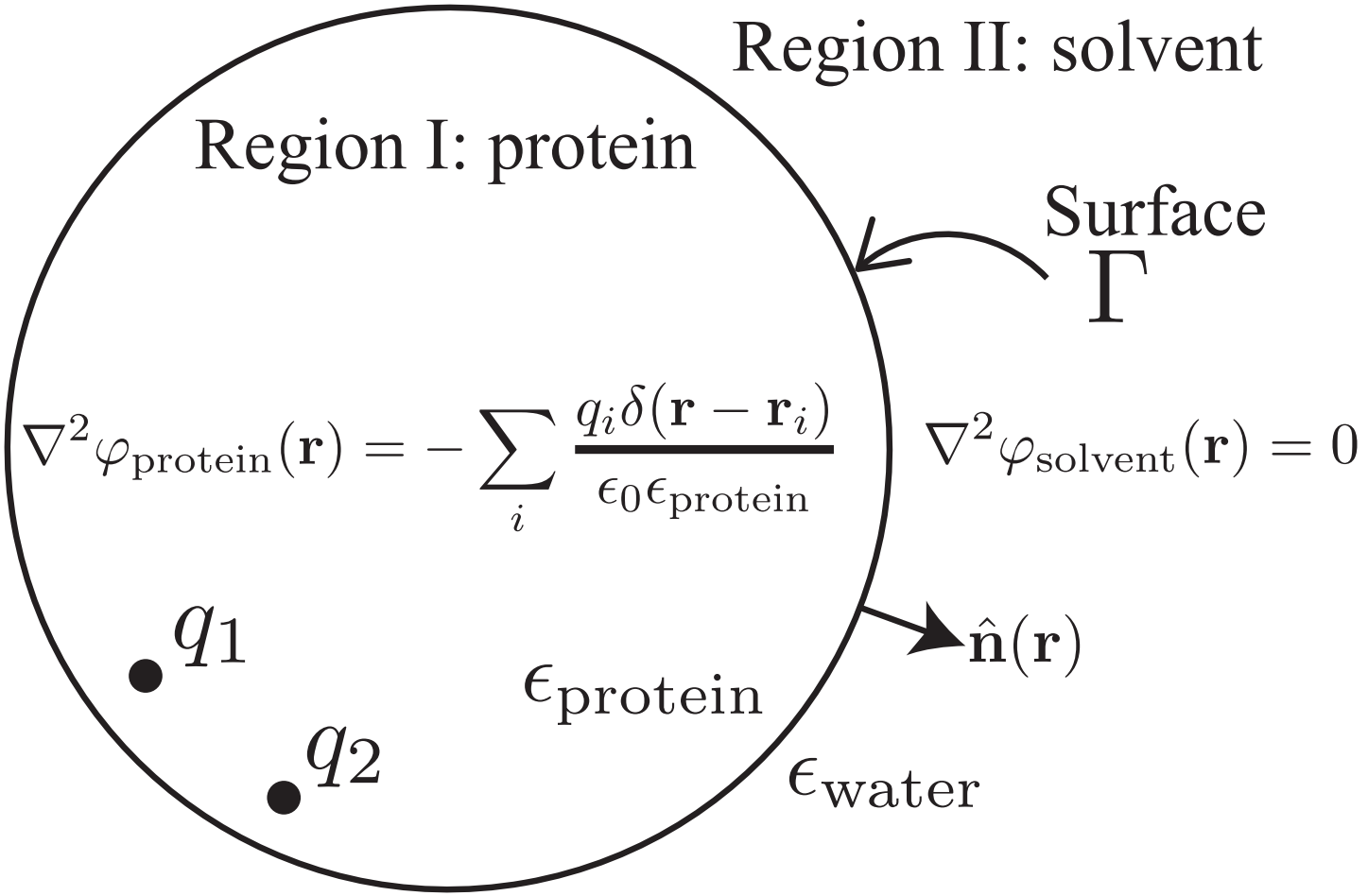
## The Natural World




Induced Surface Charge on Lysozyme

# Bioelectrostatics
## Physical Model

### Electrostatic Potential $\phi$



# Bioelectrostatics
## Mathematical Model

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

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

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

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

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However, a given atom

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

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

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## Problems

Why is this a bad model?

- Ignores experimental data (crystal radii)

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# Biomolecular Modeling
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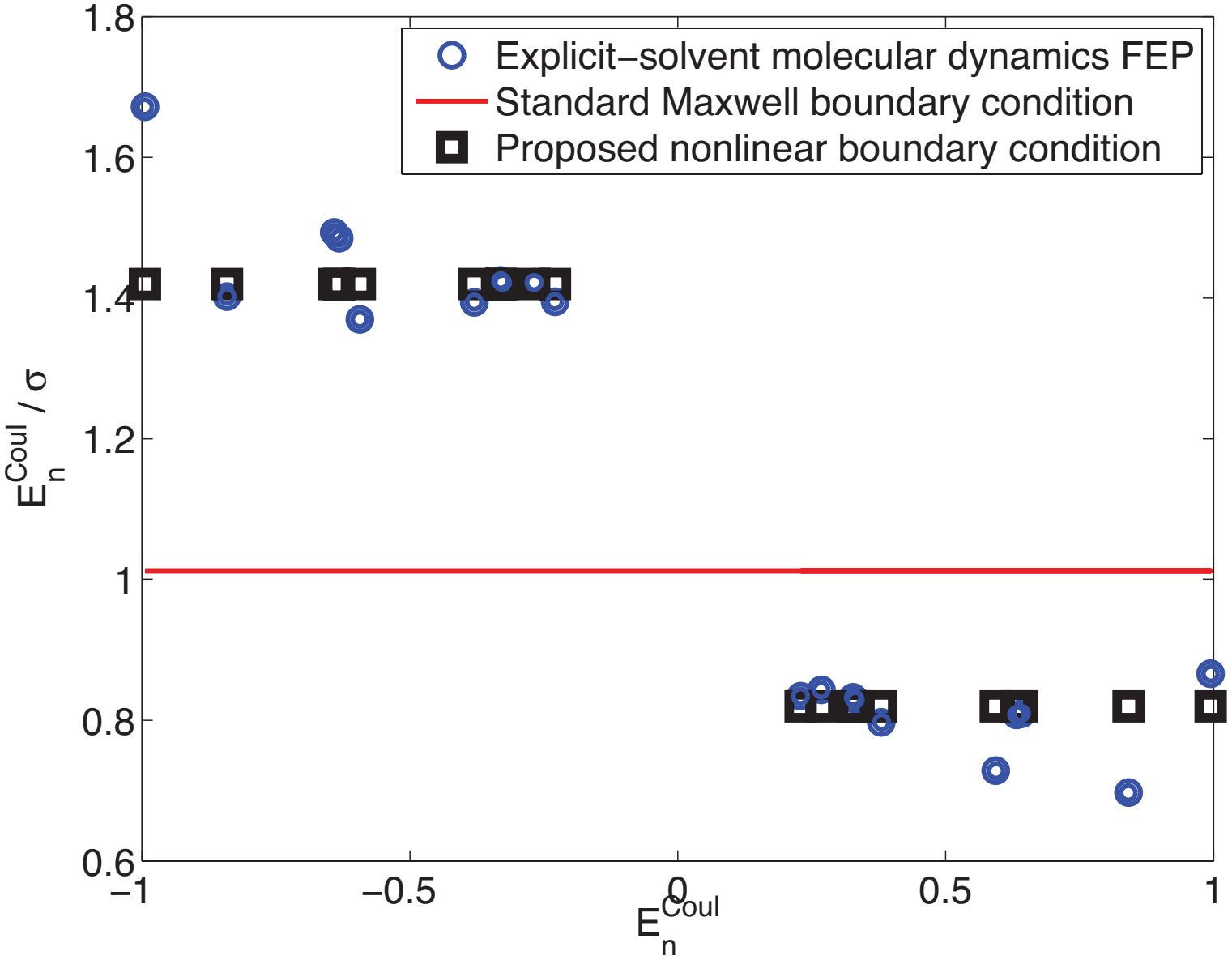
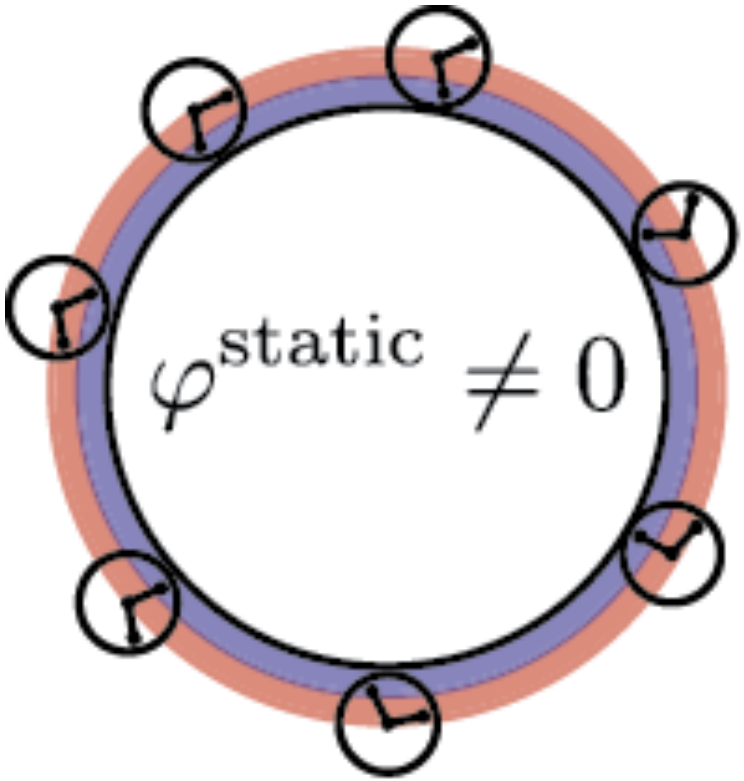
Why is this a bad model?

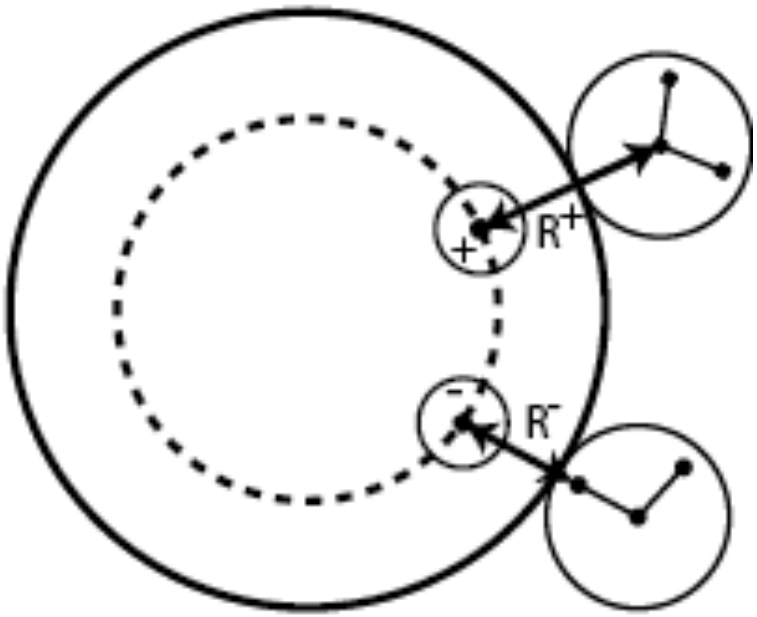
- Ignores experimental data (crystal radii)
- Not robust to solute/solvent/temperature changes
- Misses sensitivity to local electrostatic conditions
- Gives nonsense for the entropy

# Origins of Electrostatic Asymmetry



# Origins of Electrostatic Asymmetry



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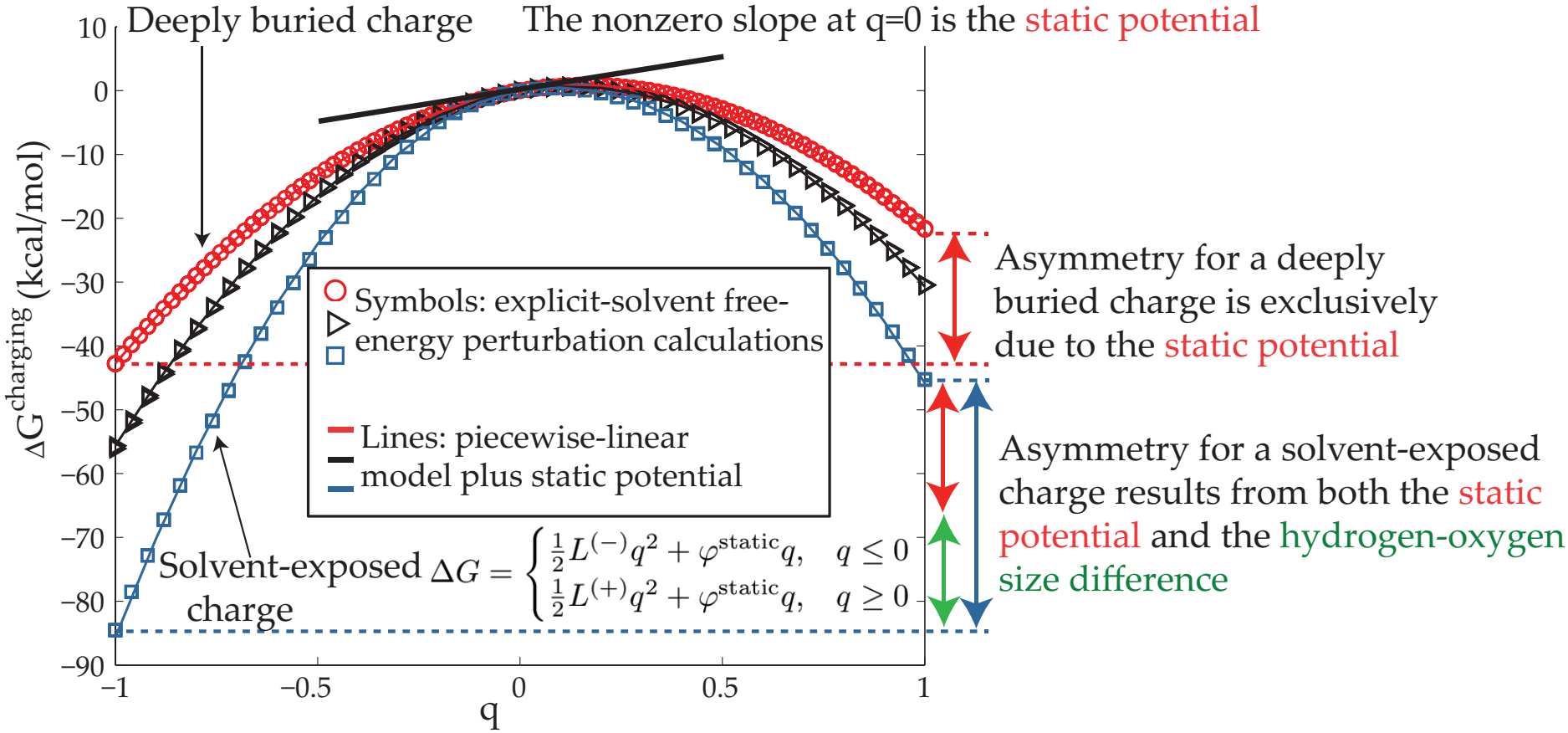


# Main Idea

## 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

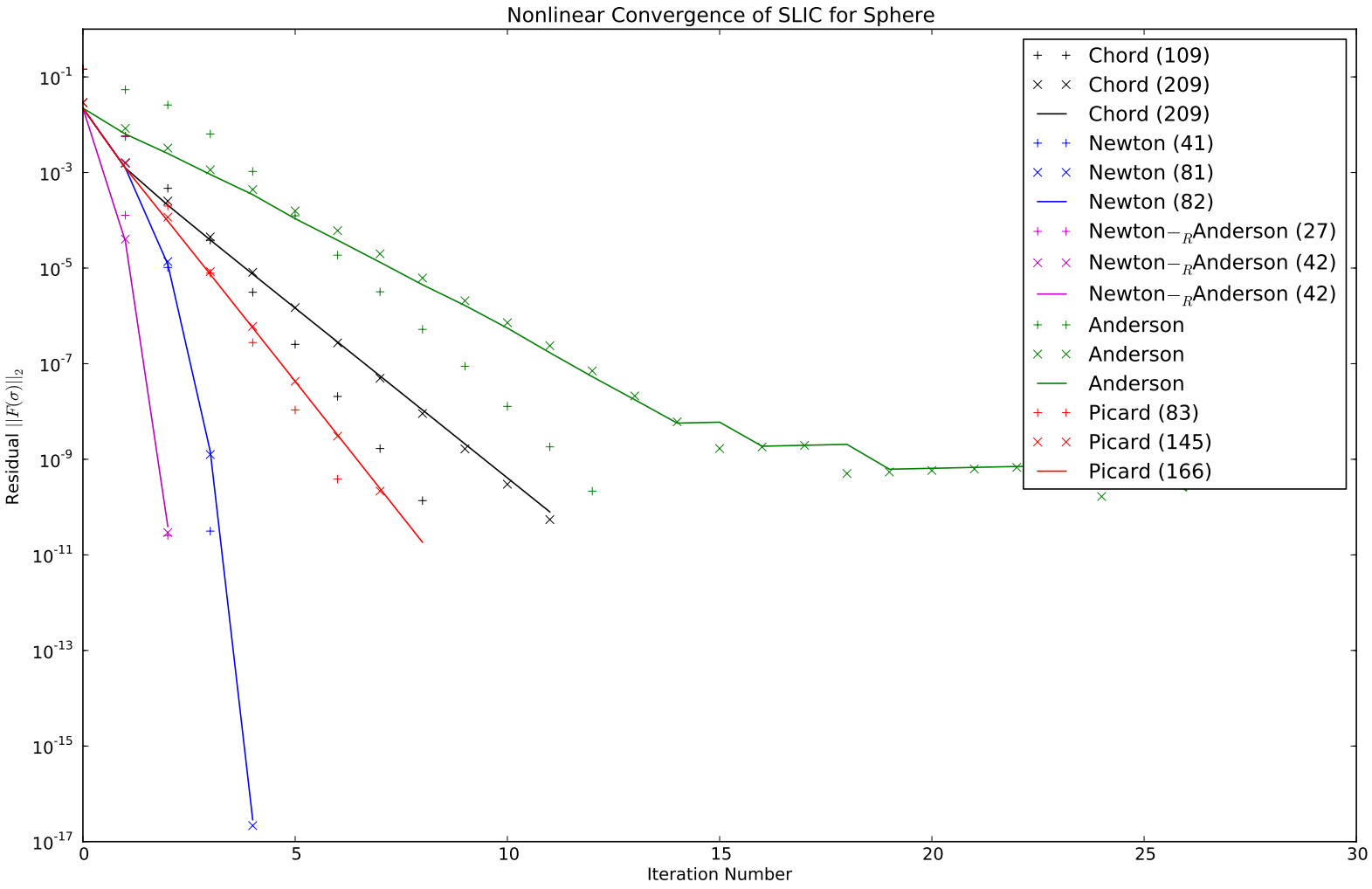
$$h(E_n) = \alpha \tanh\left(\beta E_n - \gamma\right) + \mu$$

where

- $\alpha$ Size of the asymmetry
- $\beta$ Width of the transition region
- $\gamma$ The transition field strength
- $\mu$ 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

$$F(u) = b$$

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```
-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

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

# 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

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

# Nonlinear Solvers

If we are solving

$$F(u) = b$$

with Newton $-_R$ Generalized Broyden Method

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

# Nonlinear Solvers

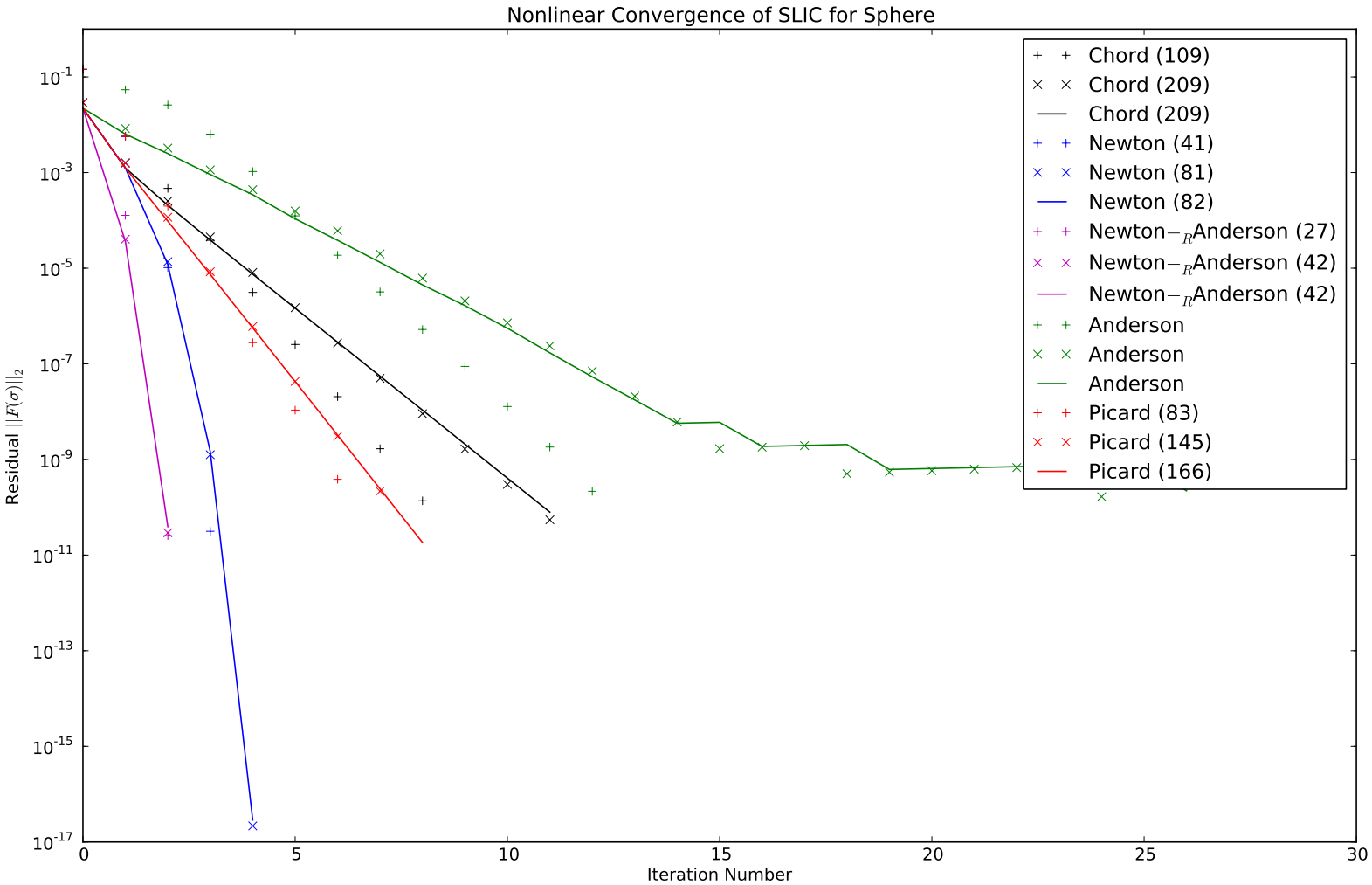
If we are solving

$$F(u) = b$$

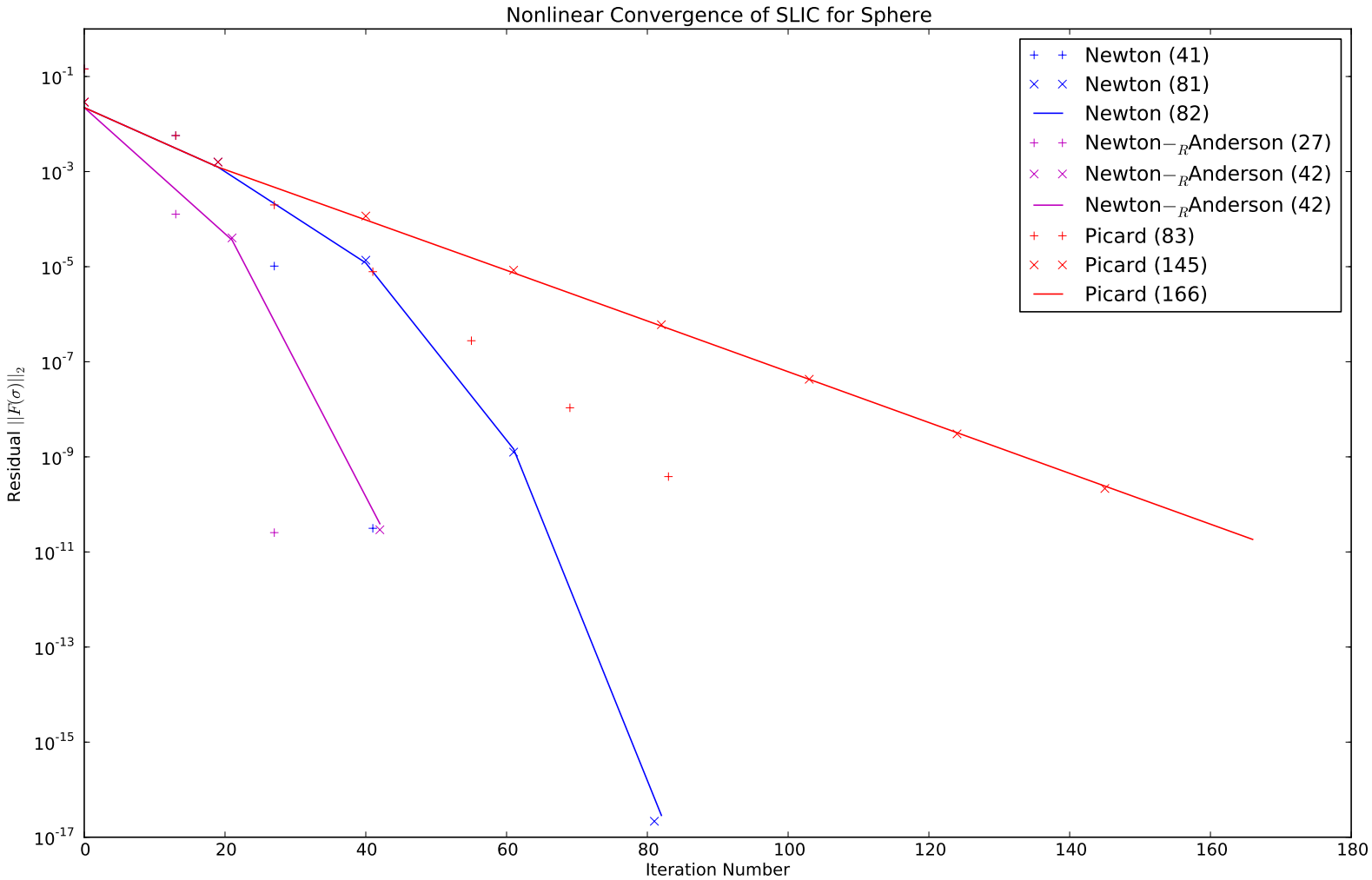
with Newton $-_R$ Generalized Broyden Method

```
-snes_type newtonls
-snes_linesearch_type basic
-npc_snes_type ngmres
-npc_snes_max_it 2
```

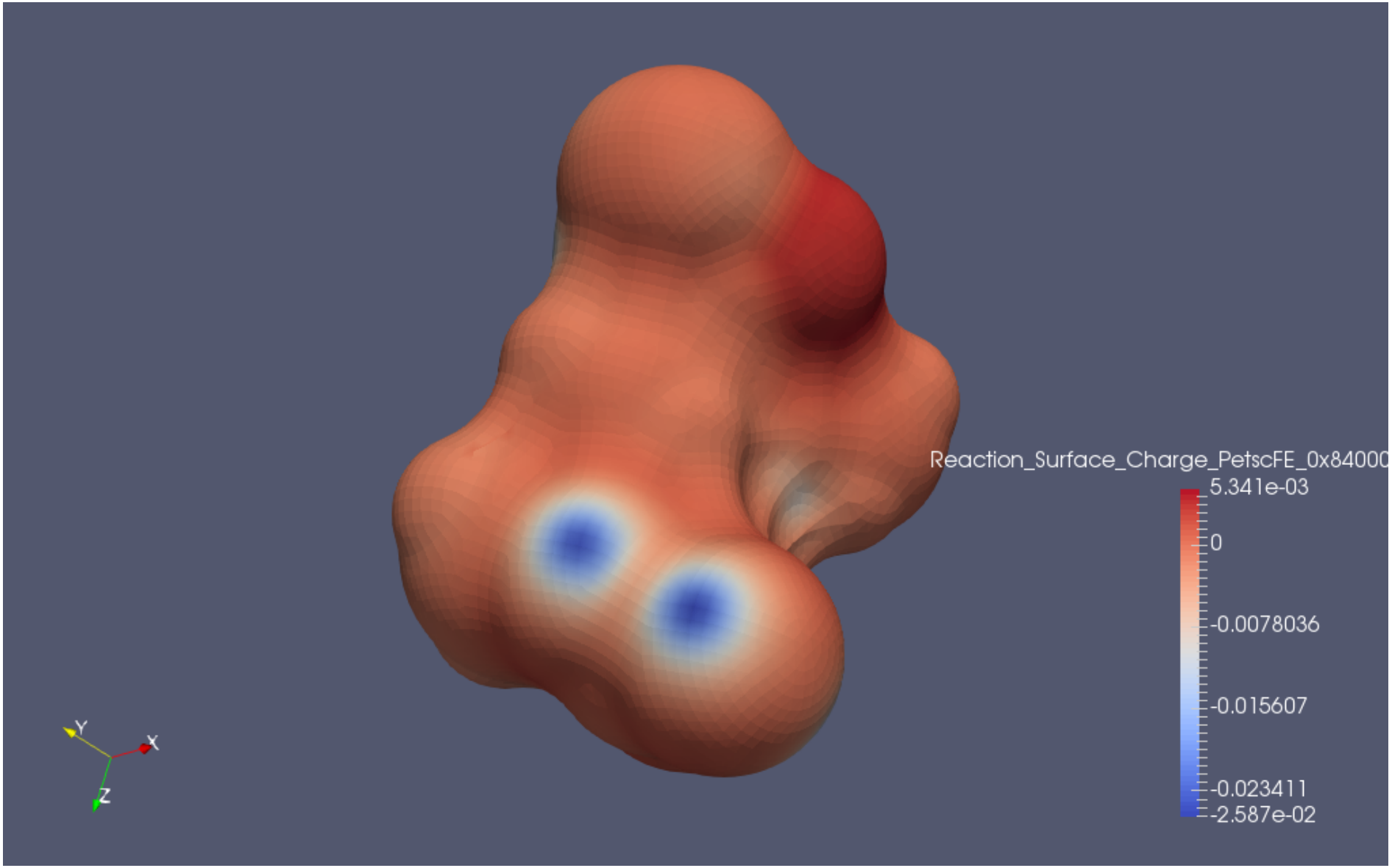
# Solving SLIC
## Sphere



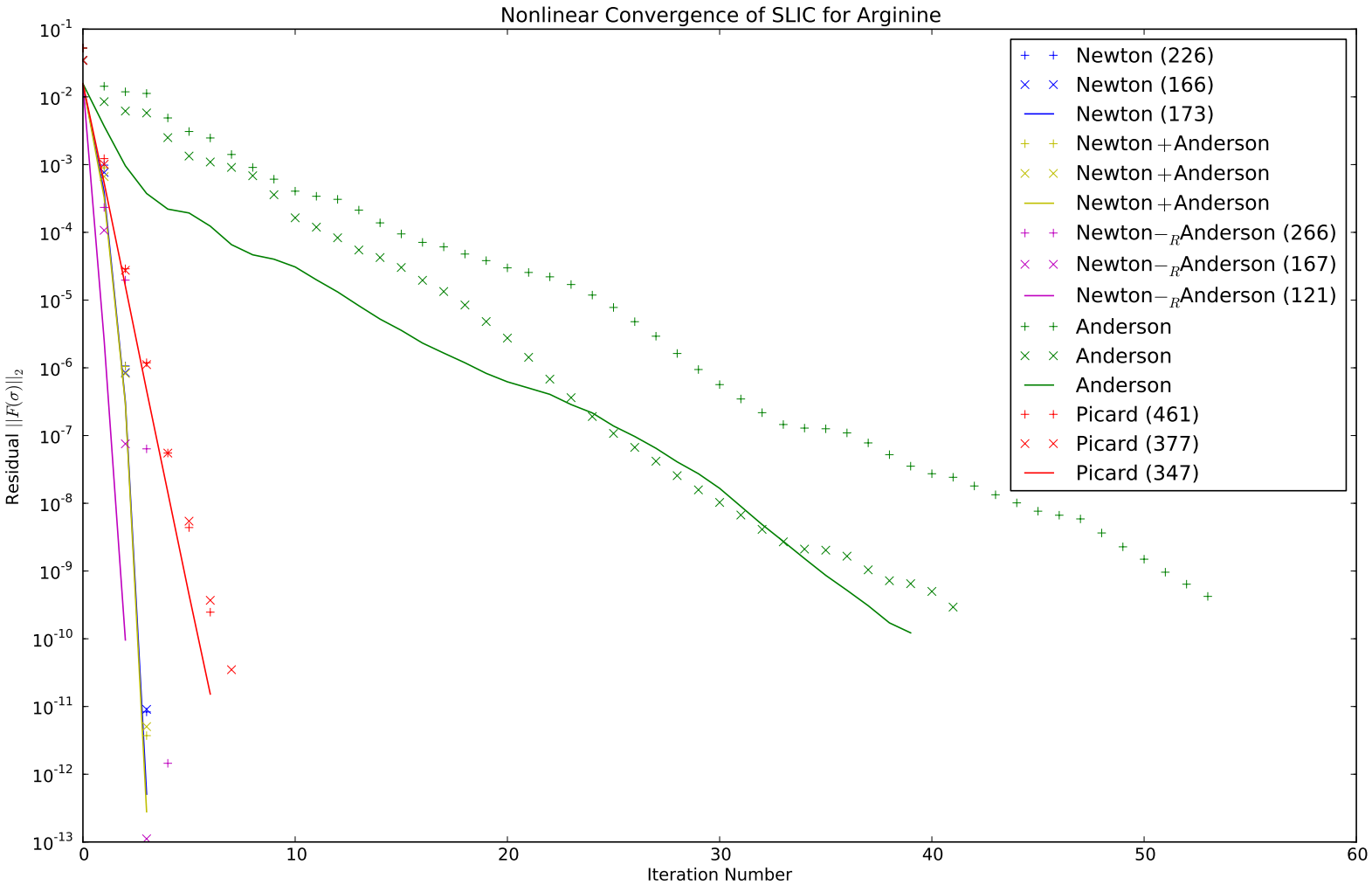
# Solving SLIC
## Sphere



# 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



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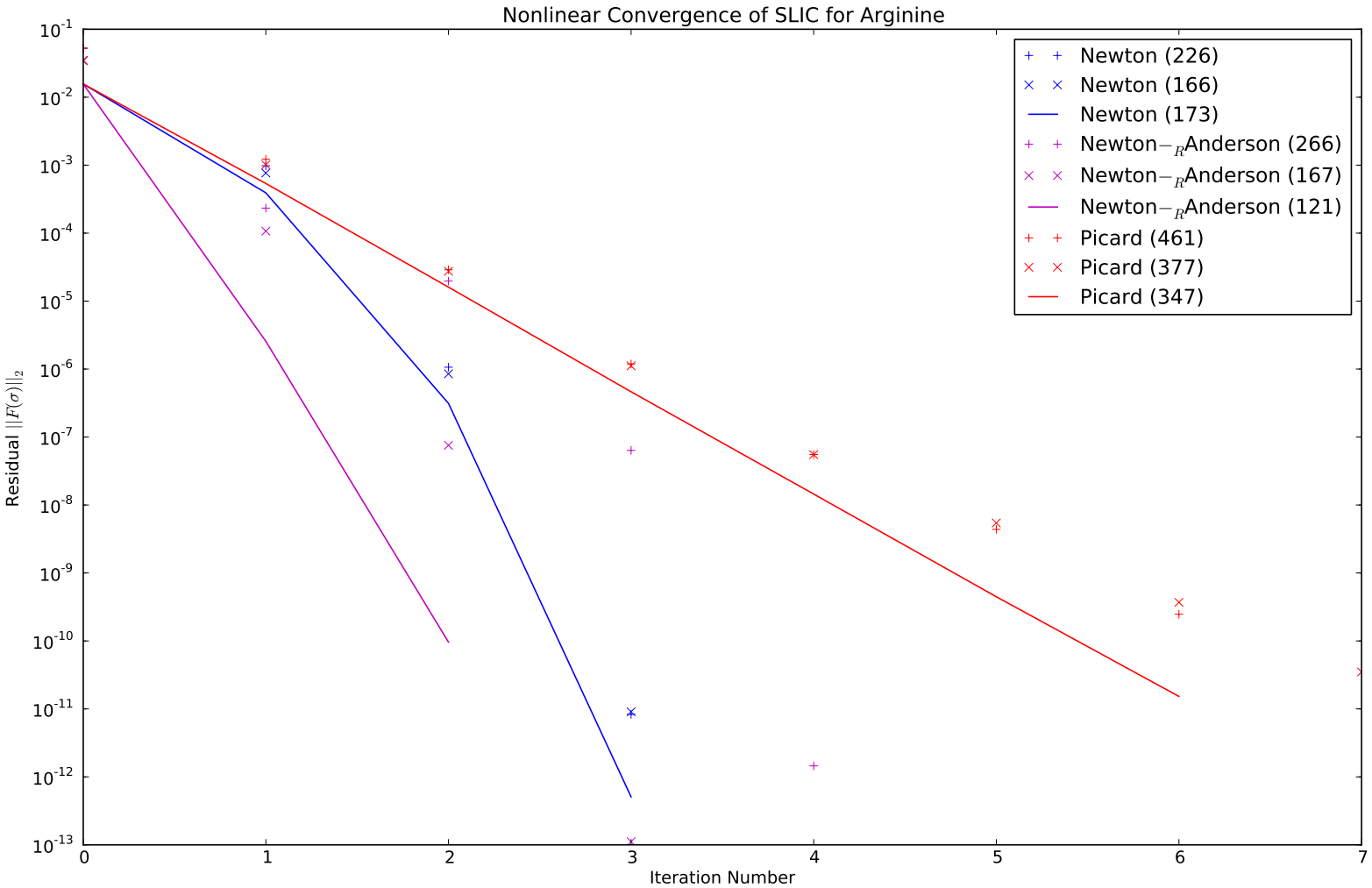
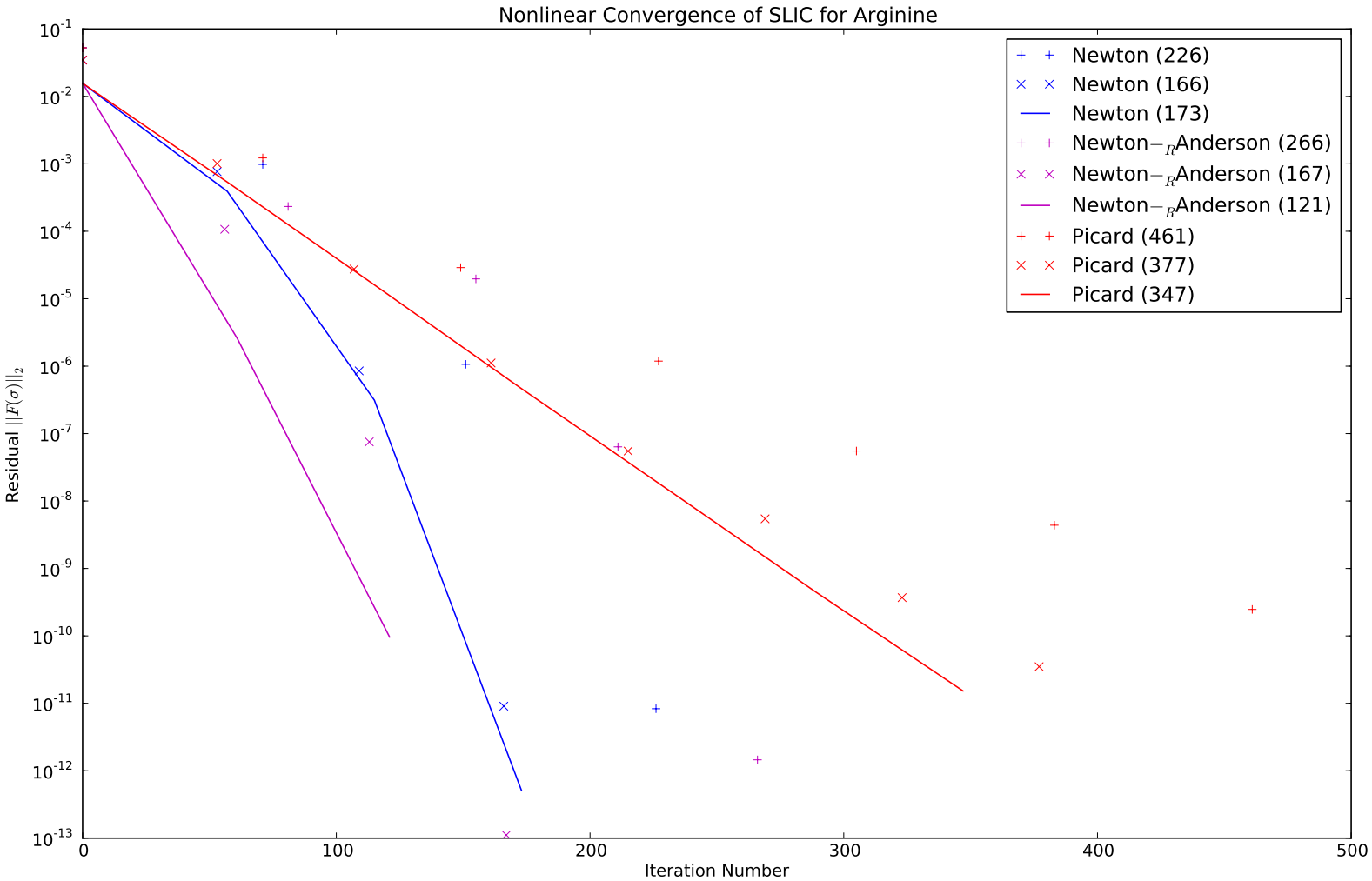
## Arginine



# Solving SLIC
## Arginine



# Outline

# Main Conclusion

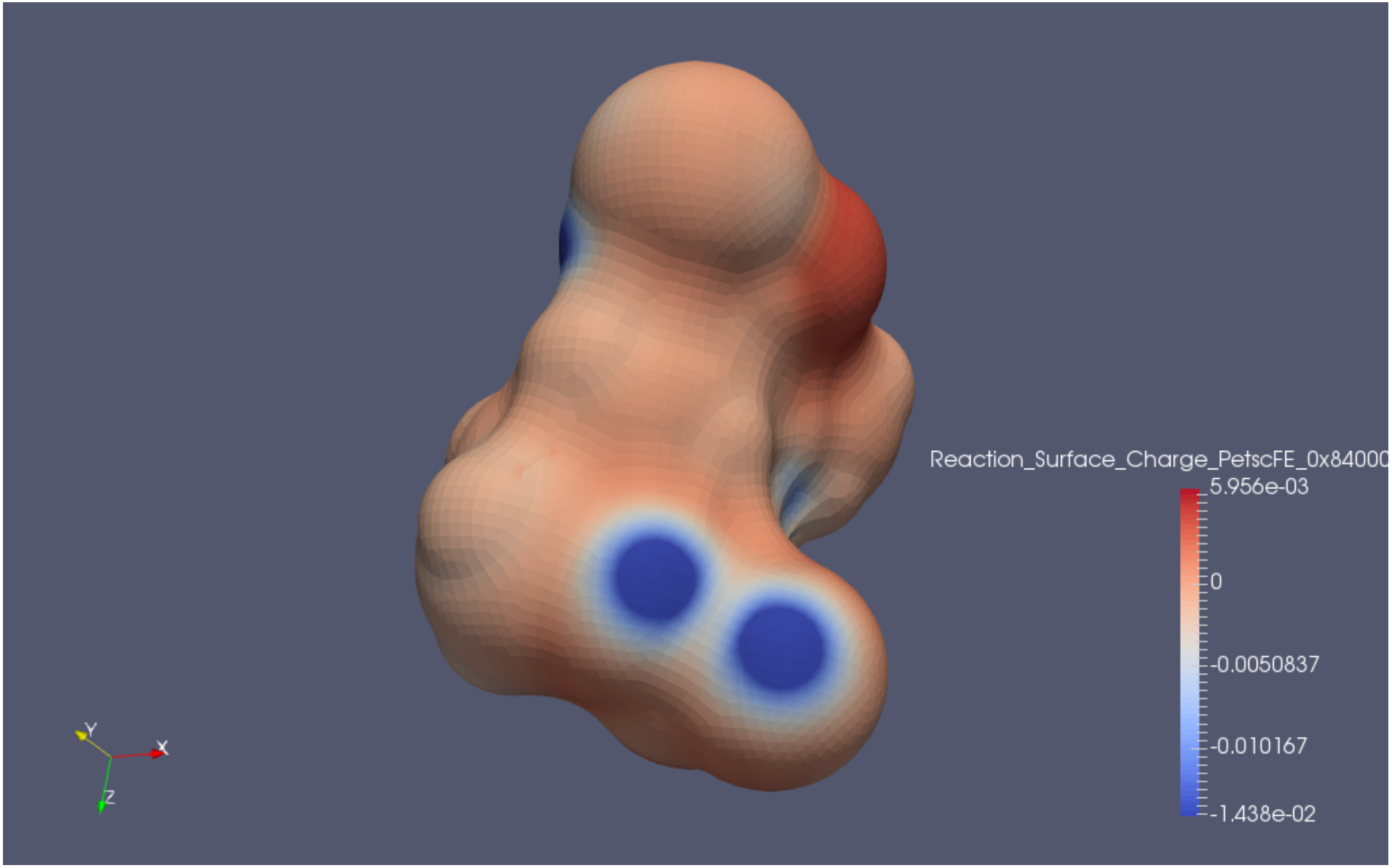
Nonlinear Preconditioning

can lead to significant speedups,

and is accessible without recoding.

# Charge Distribution

## Maxwell



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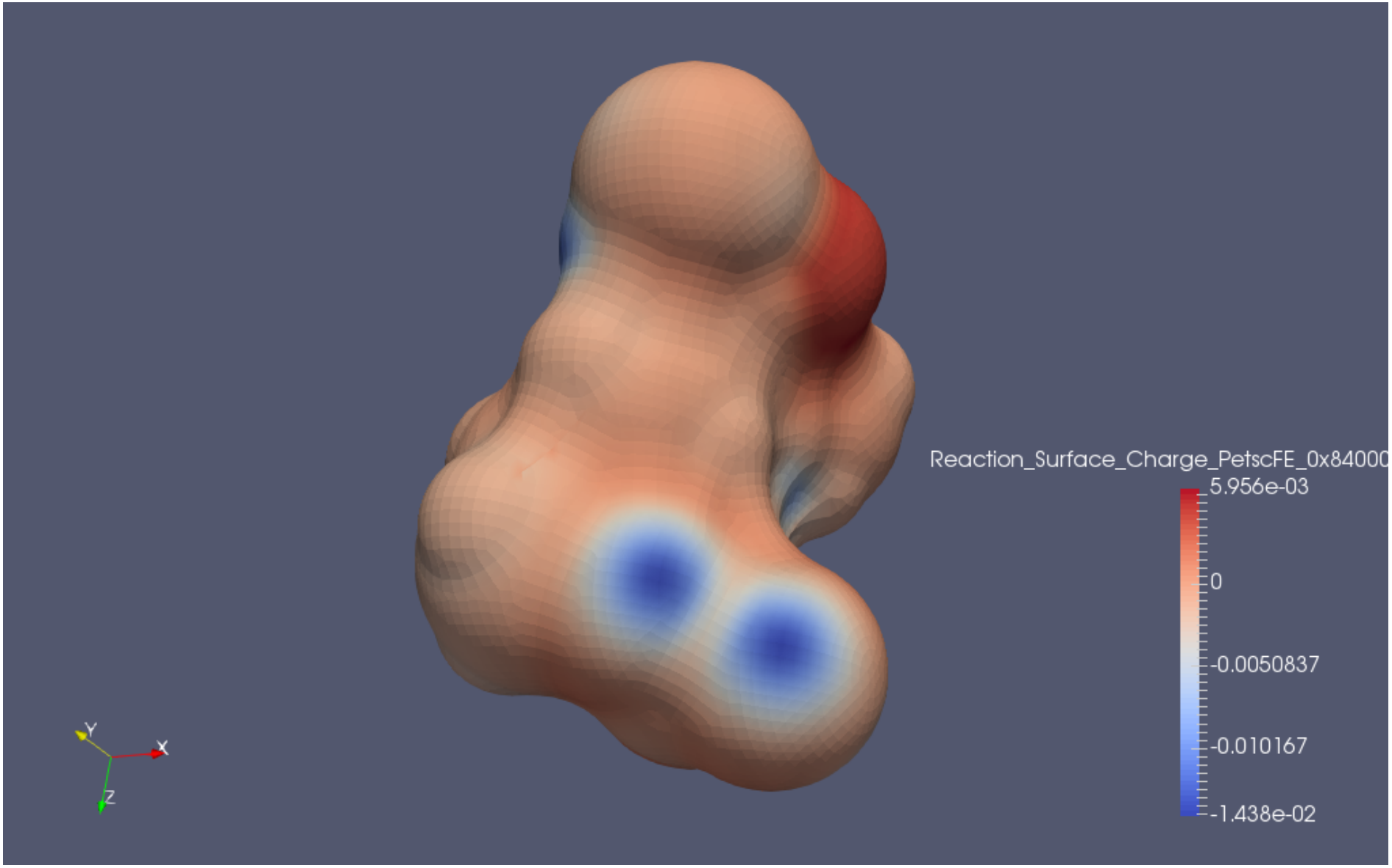
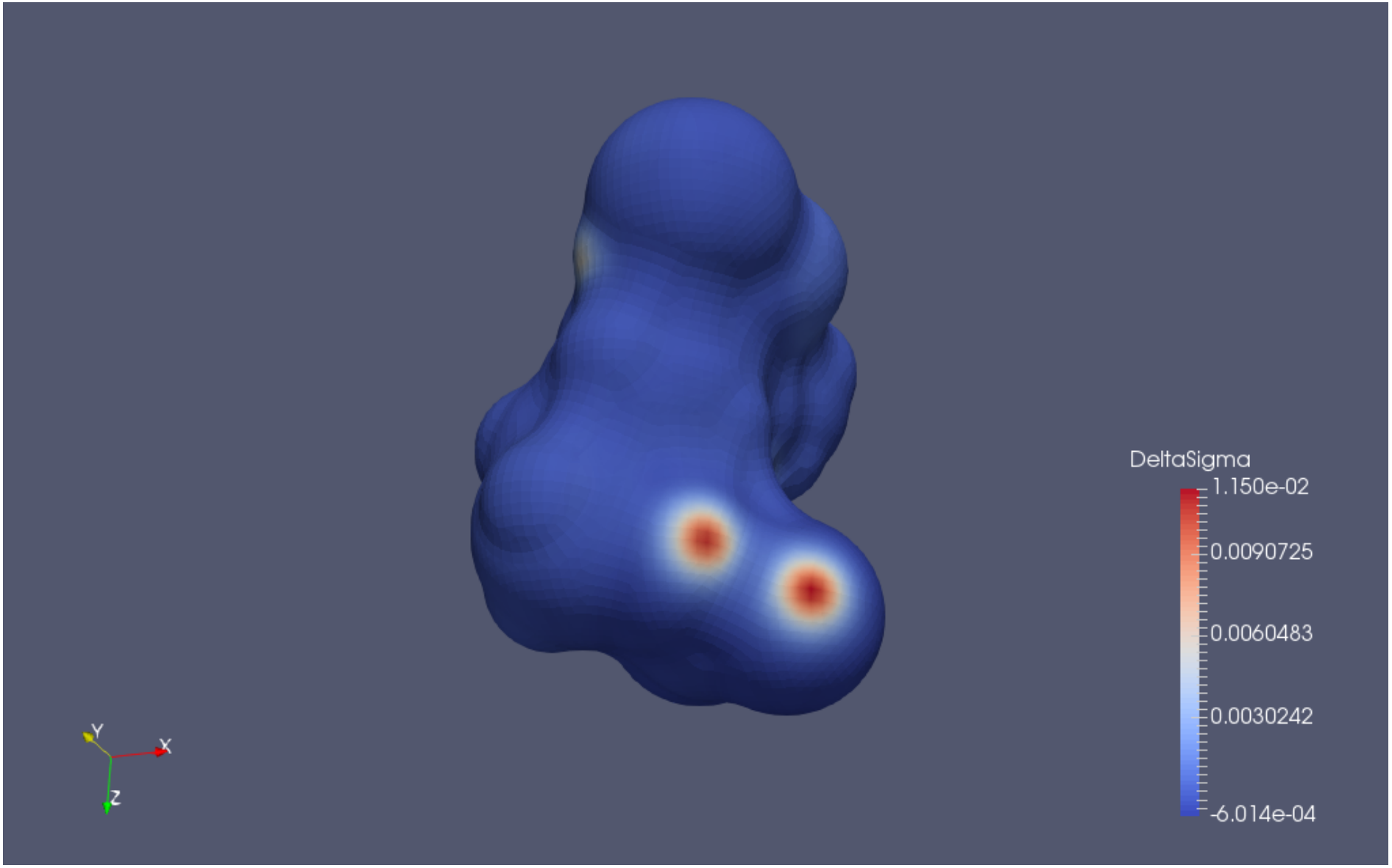
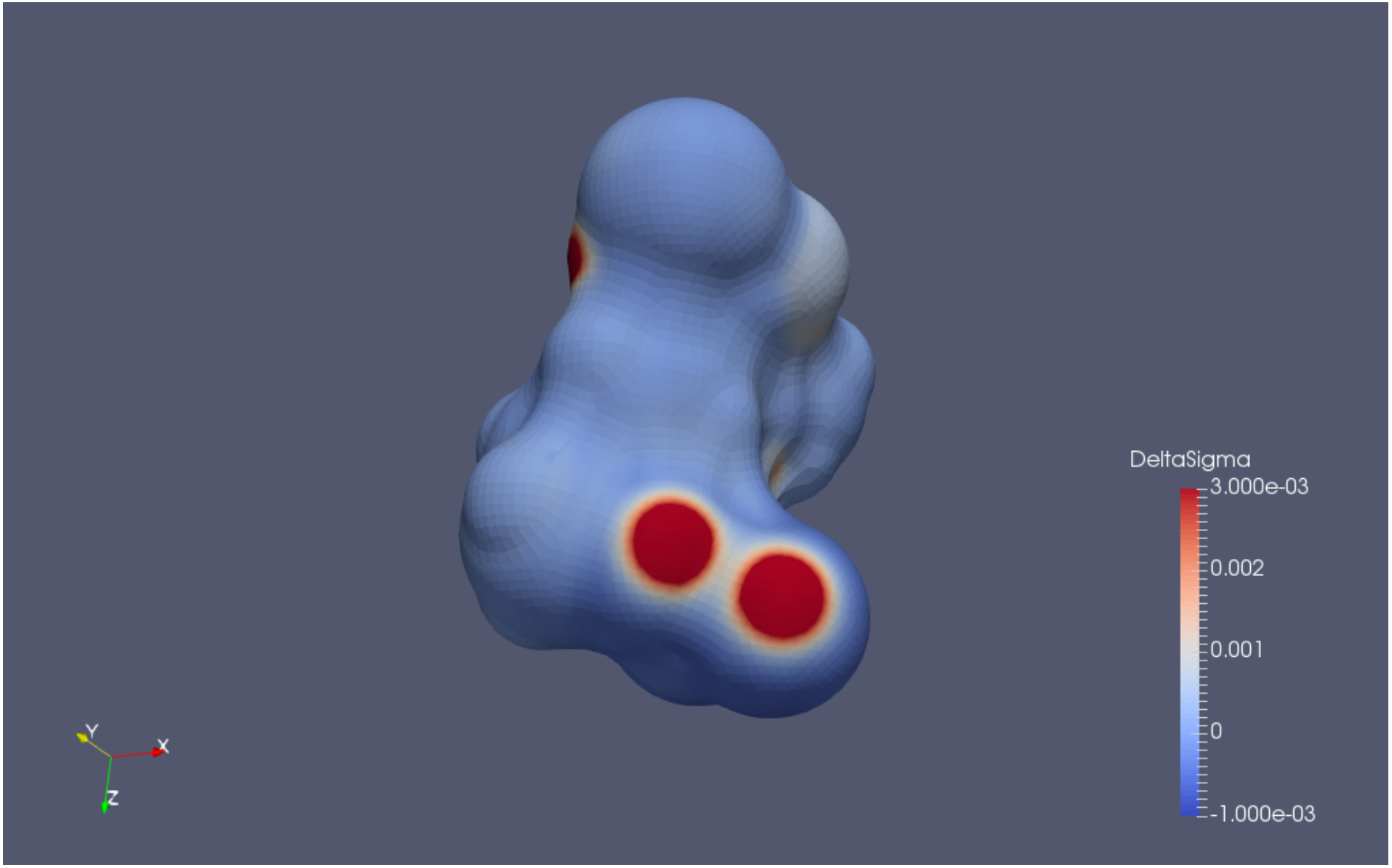


# Charge Distribution
## Difference



# 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