Improved Solvation Models using Boundary Integral Equations

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Engineering Faculty Research Highlights
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Main Point

Solvation computation can benefit from

operator simplification,

and non-Poisson models.

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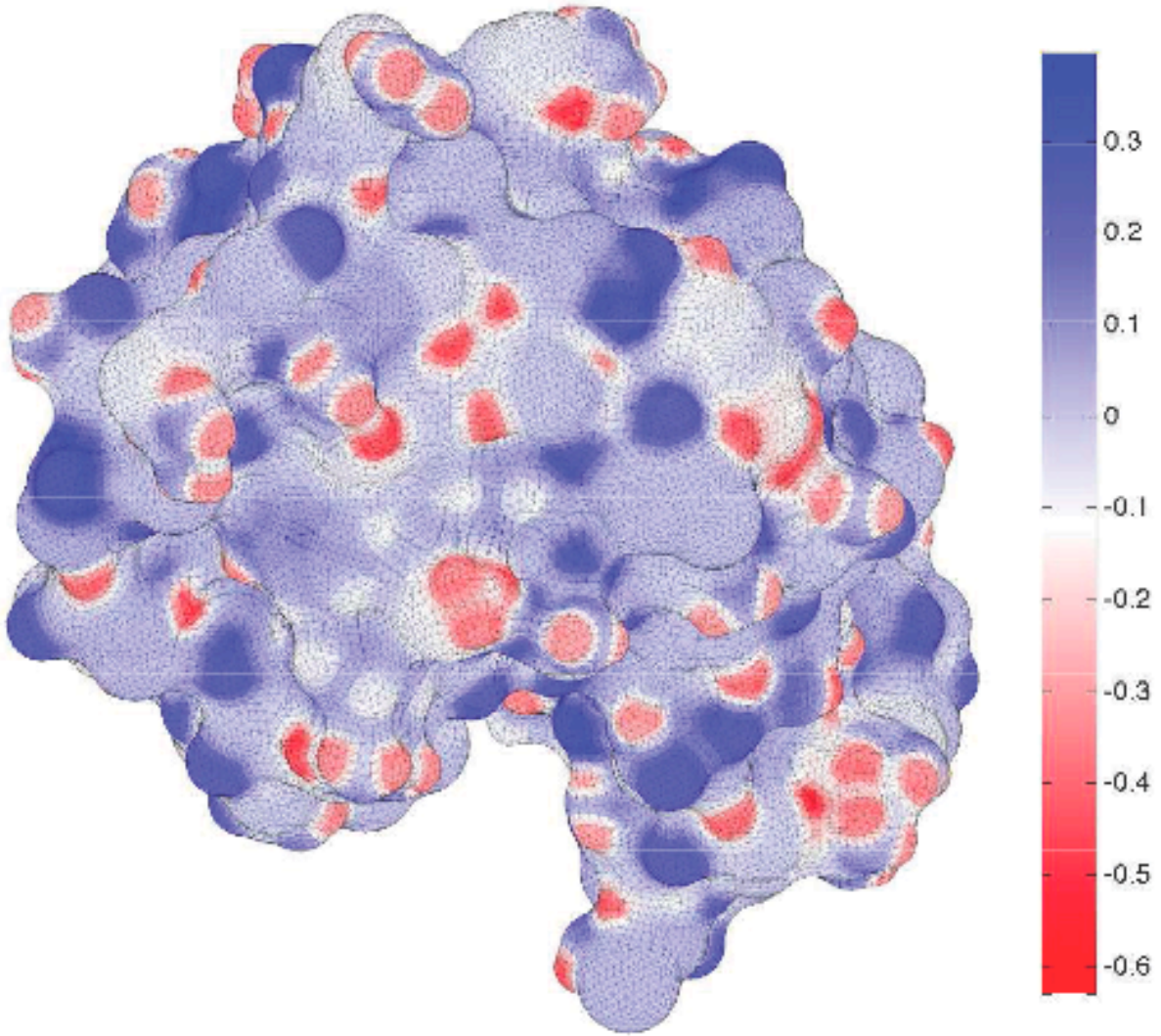
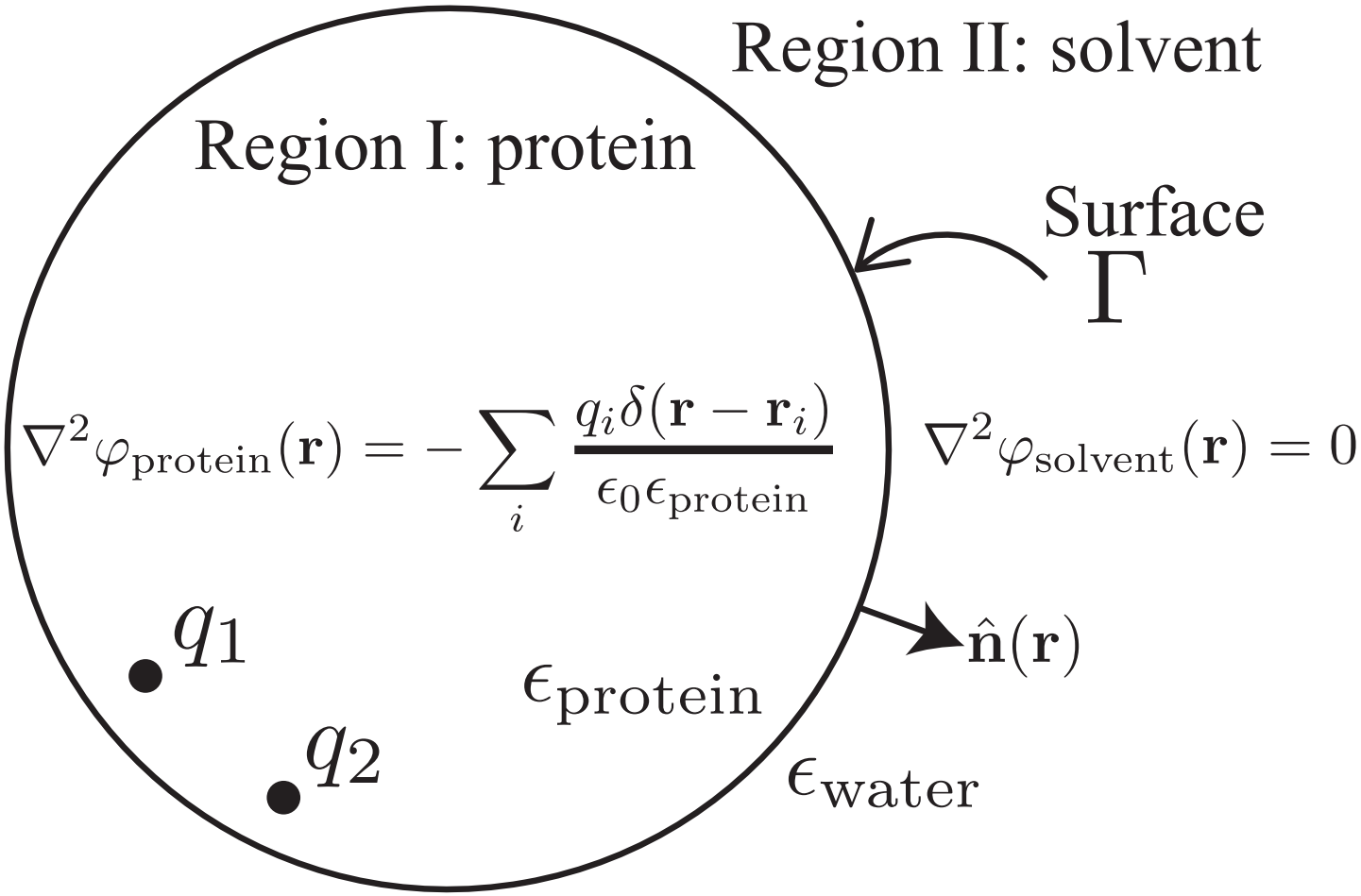
Bioelectrostatics

The Natural World



Induced Surface Charge on Lysozyme

Electrostatic Potential ϕ



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

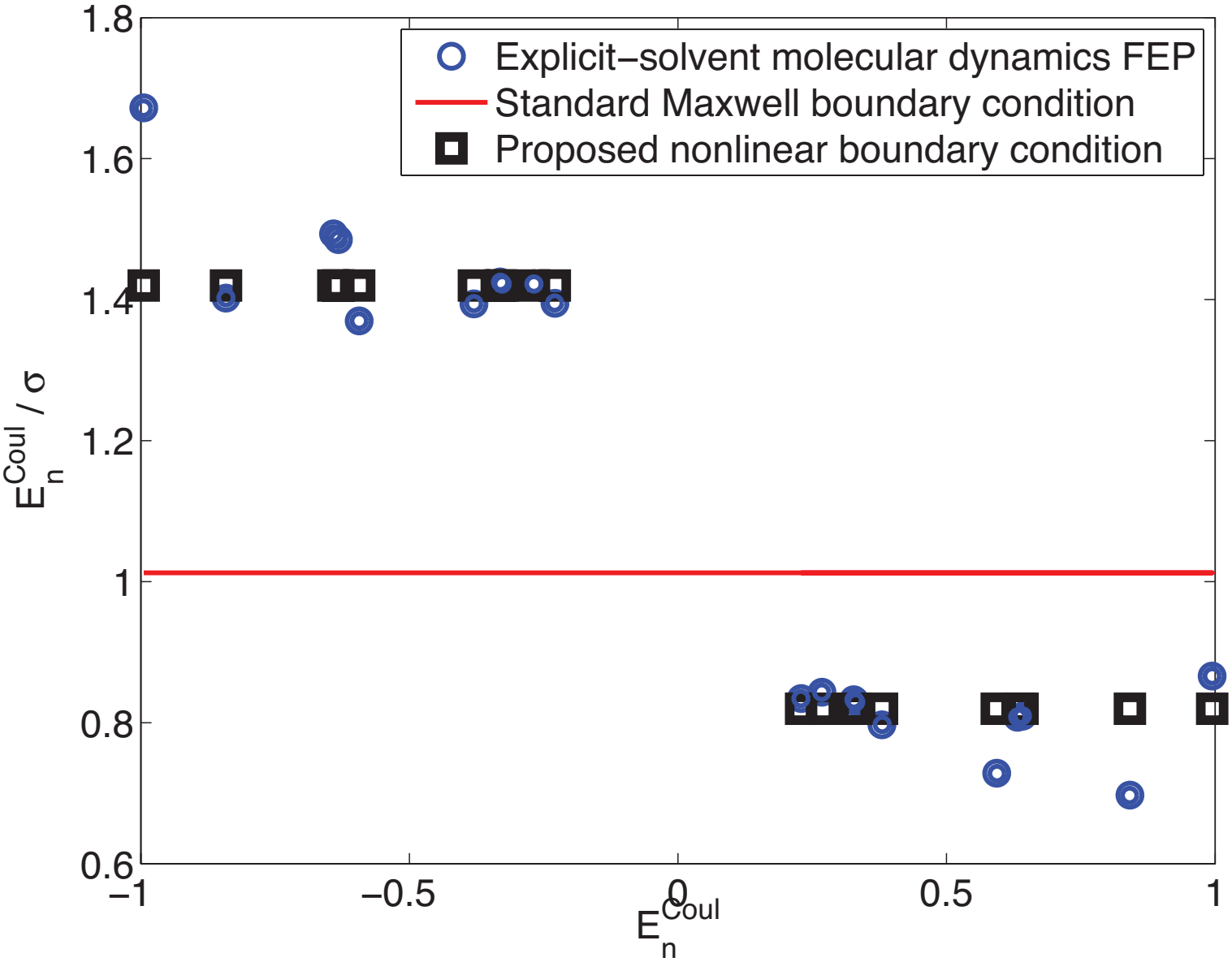
$$\sigma(\vec{r}) + \hat{\epsilon} \int_\Gamma \frac{\partial}{\partial n(\vec{r})} \frac{\sigma(\vec{r}')d^2\vec{r}'}{4\pi||\vec{r} - \vec{r}'||} = -\hat{\epsilon} \sum_{k=1}^{Q} \frac{\partial}{\partial n(\vec{r})} \frac{q_k}{4\pi||\vec{r} - \vec{r}_k||}$$

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

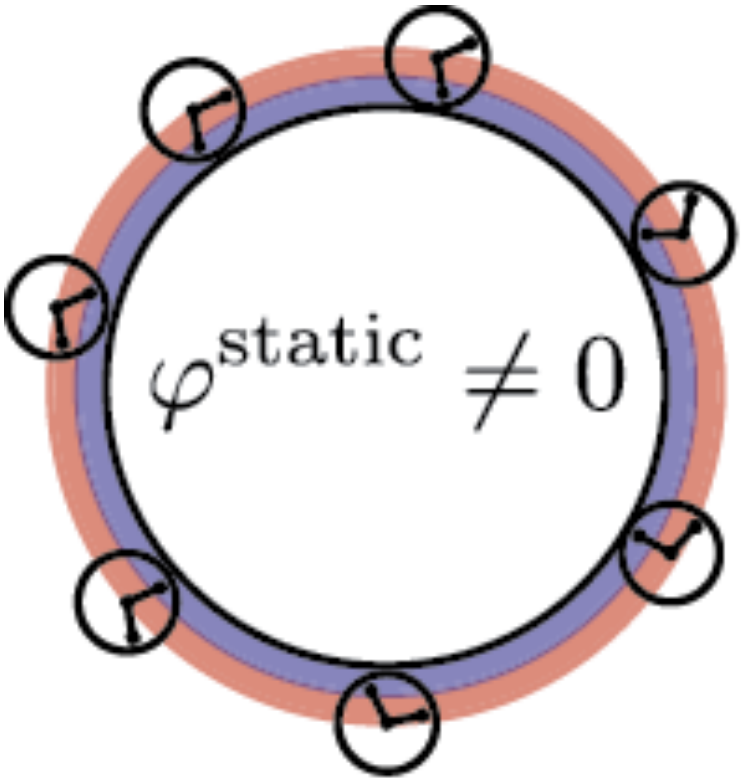
where we define

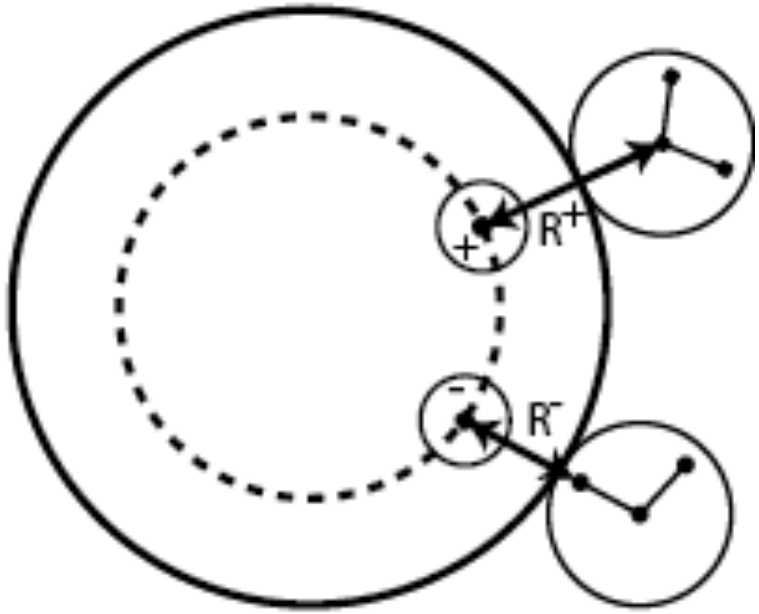
$$\hat{\epsilon} = 2\frac{\epsilon_I - \epsilon_{II}}{\epsilon_I + \epsilon_{II}} < 0$$

Origins of Electrostatic Asymmetry

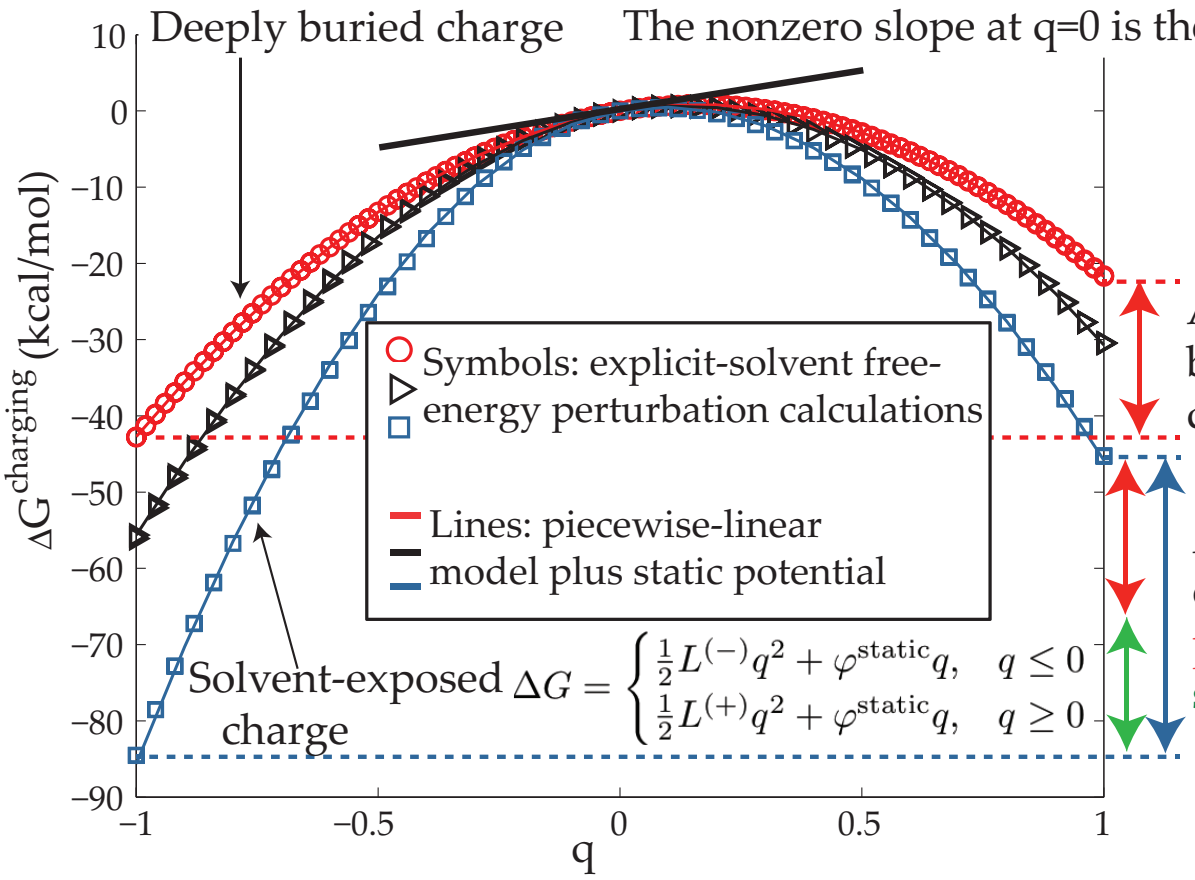


Origins of Electrostatic Asymmetry





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

Solvation-Layer Interface Condition (SLIC)

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

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

Solvation-Layer Interface Condition (SLIC)

assume the energy and radii and derive the model.

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

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.

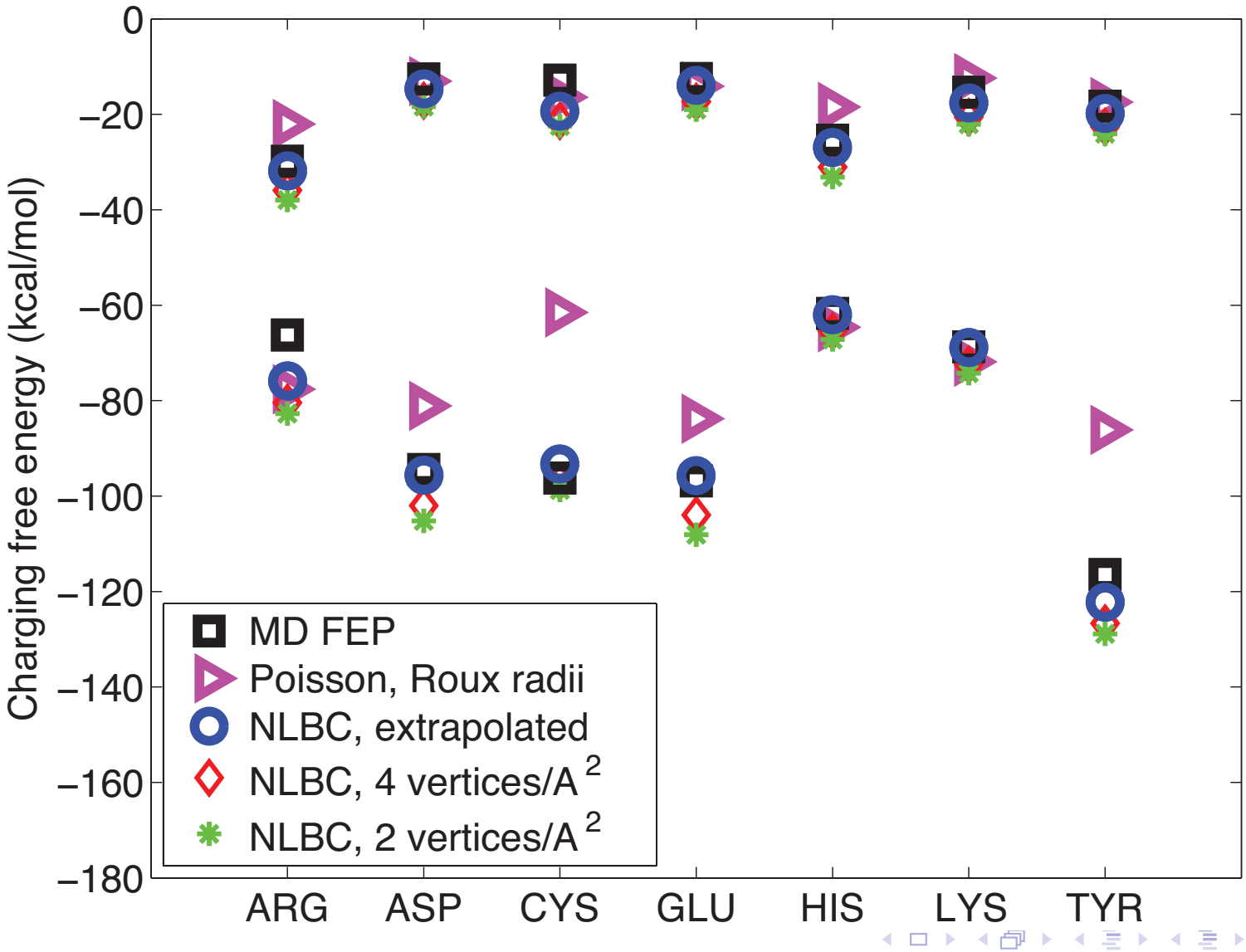
$$h(E_n) = \alpha \tanh\left(\beta E_n - \gamma\right) + \mu$$

where

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

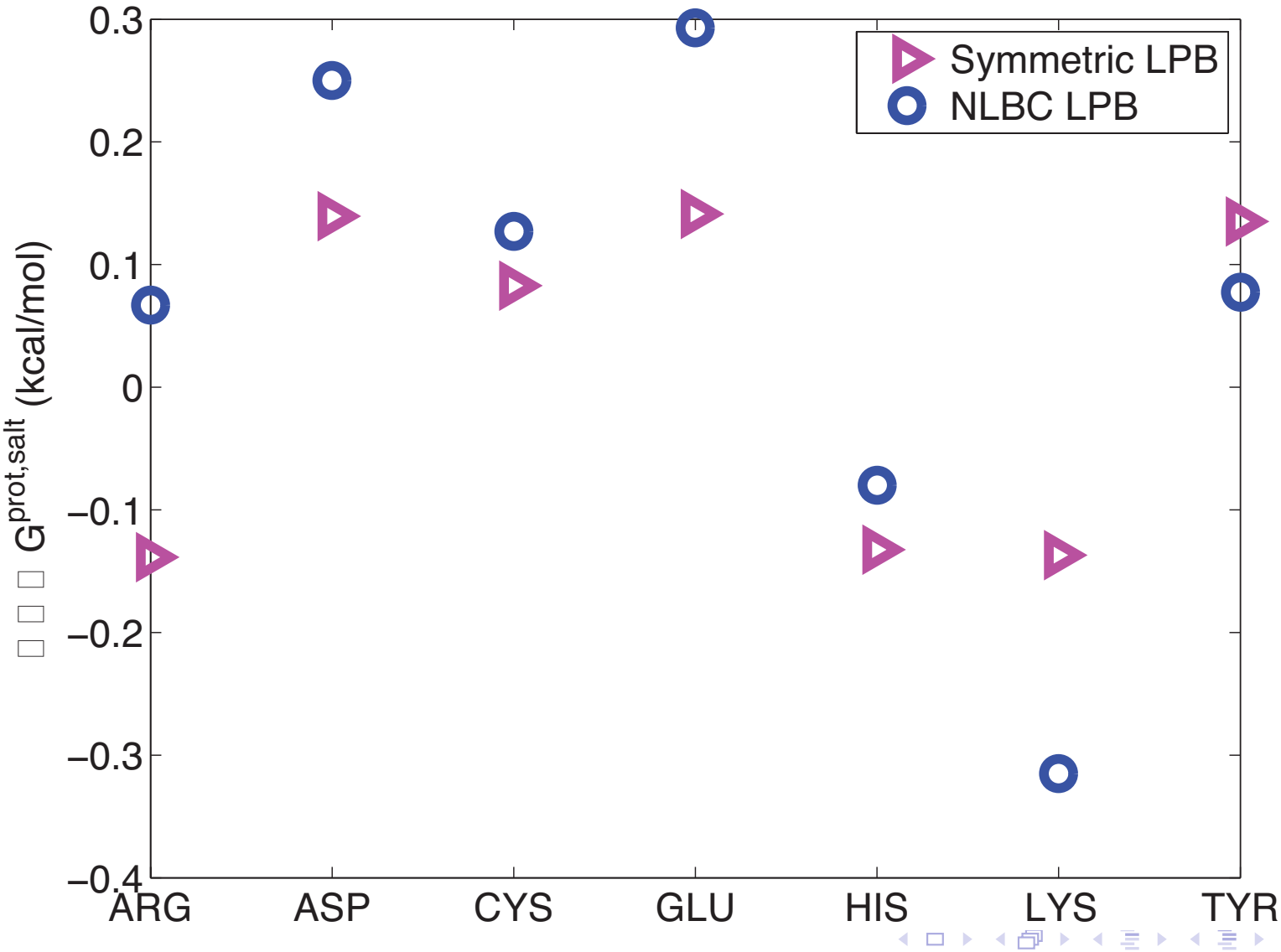
Accuracy of SLIC

Residues



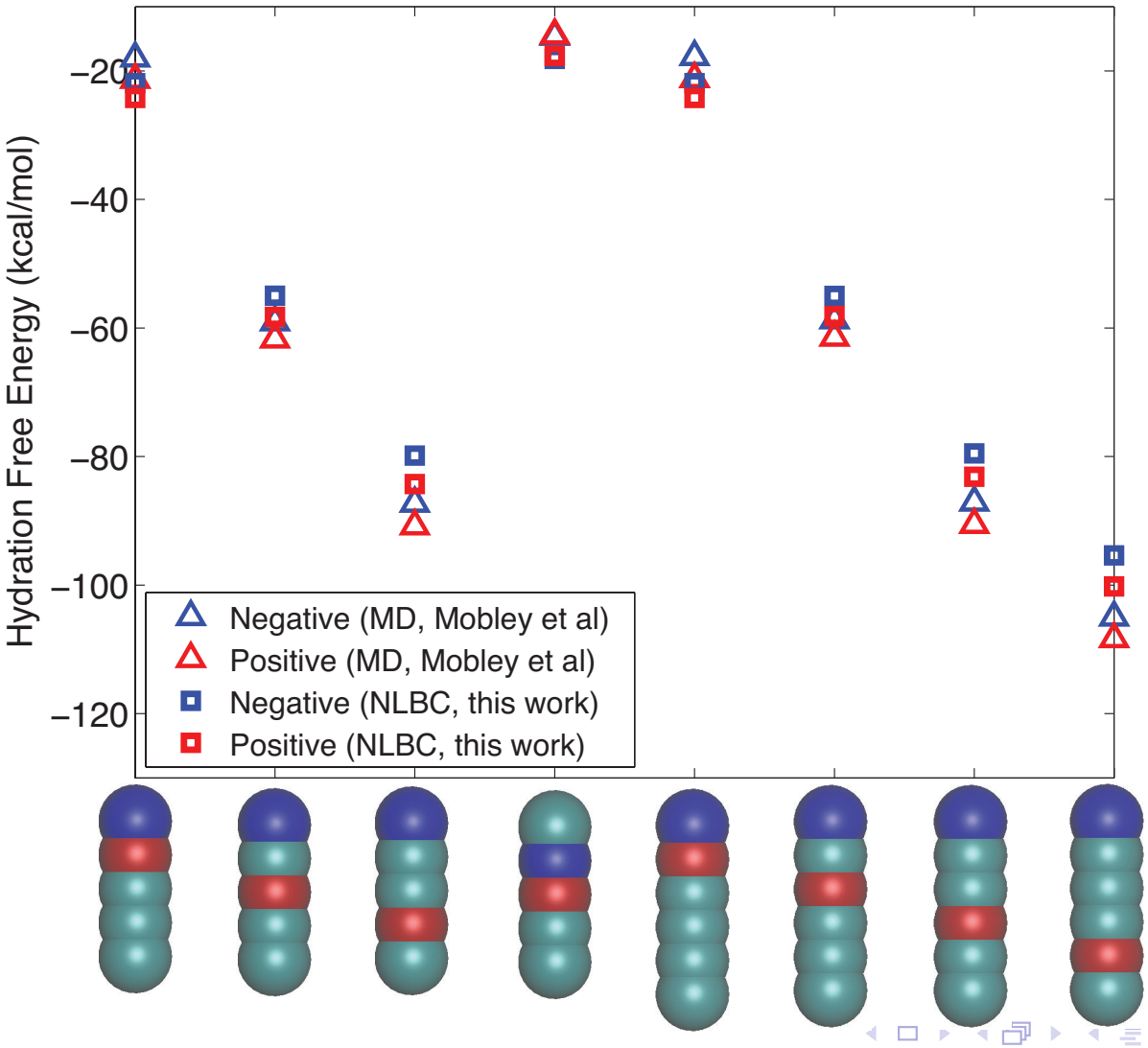
Accuracy of SLIC

Protonation



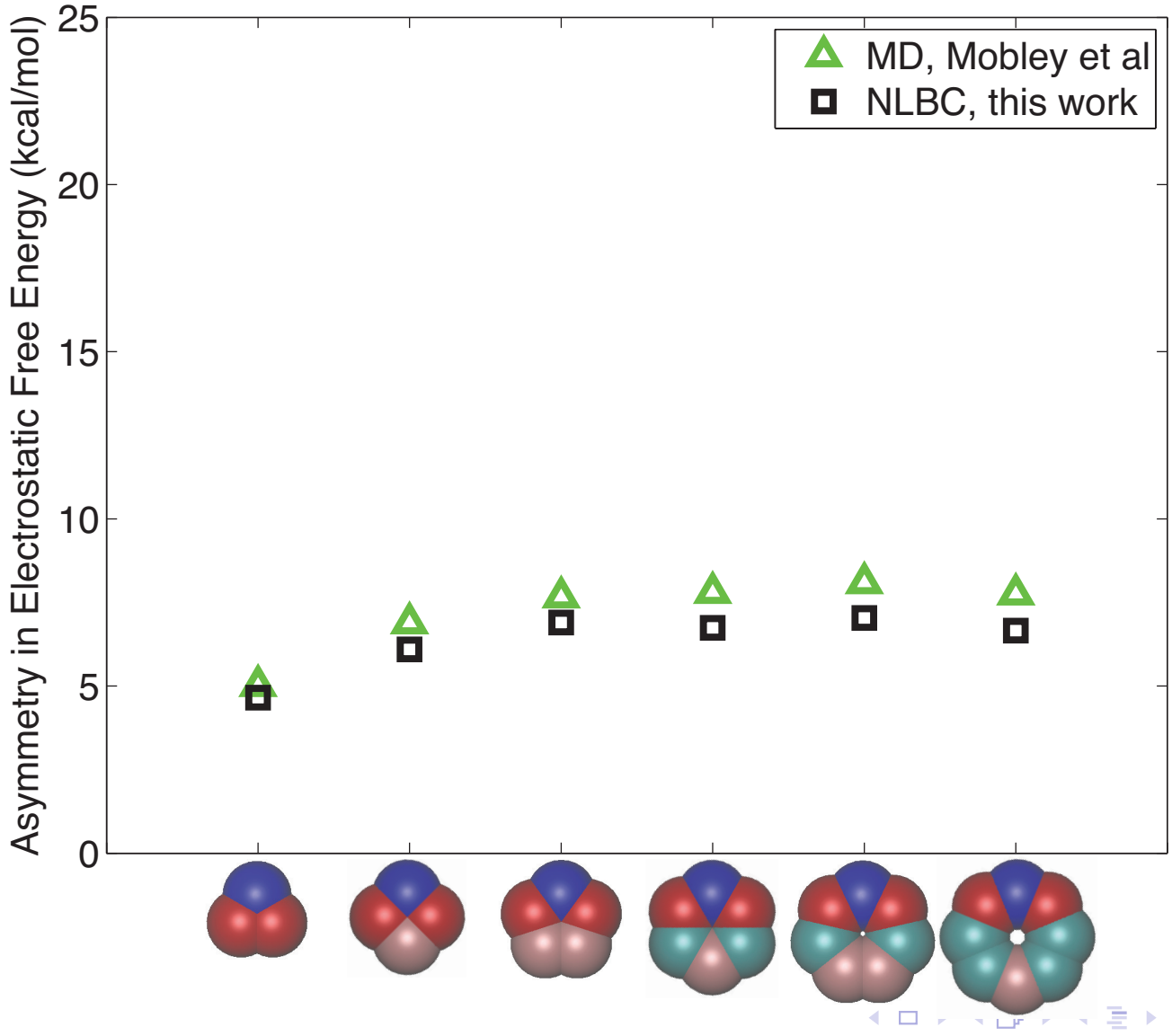
Accuracy of SLIC

Synthetic Molecules



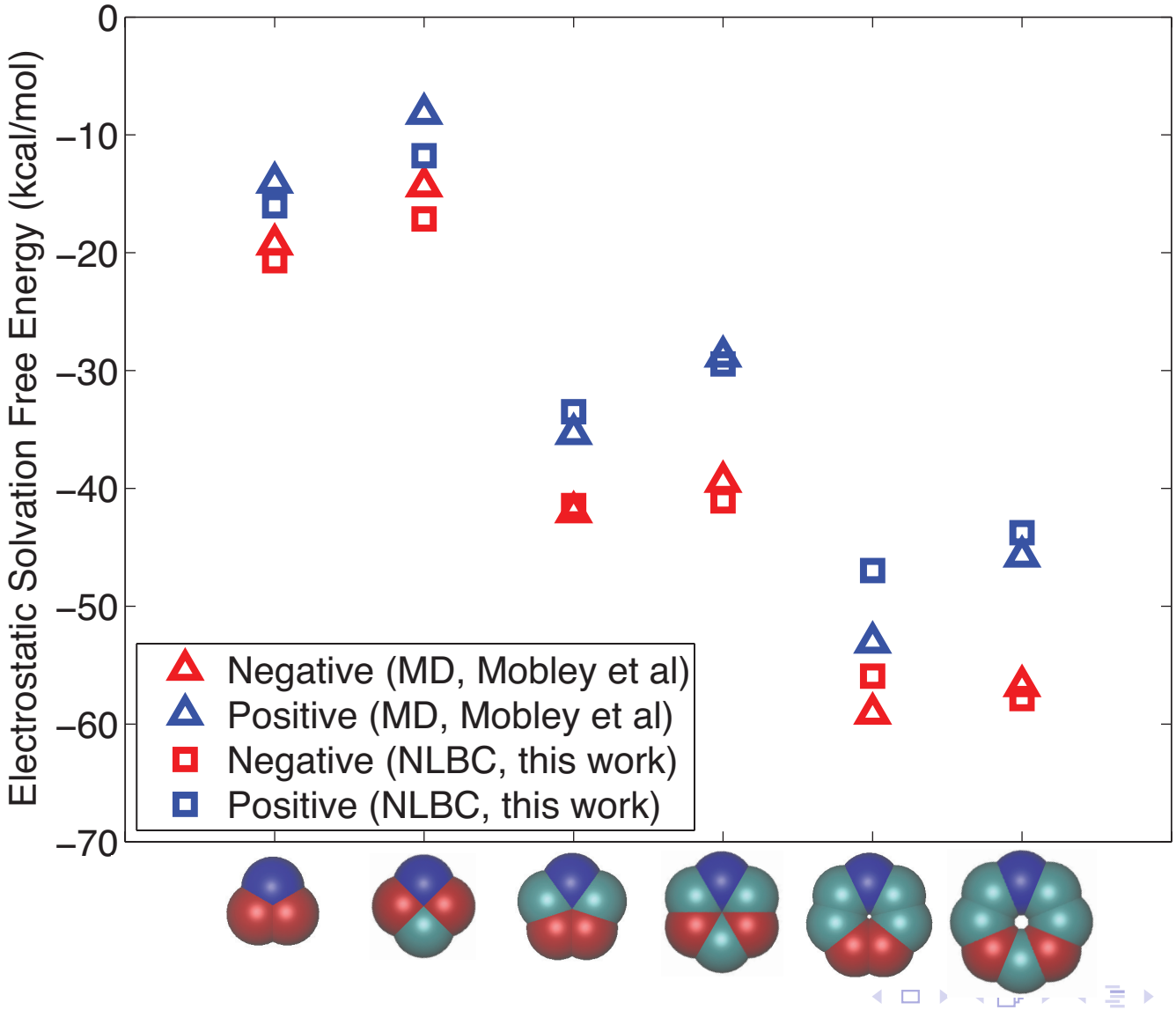
Accuracy of SLIC

Synthetic Molecules



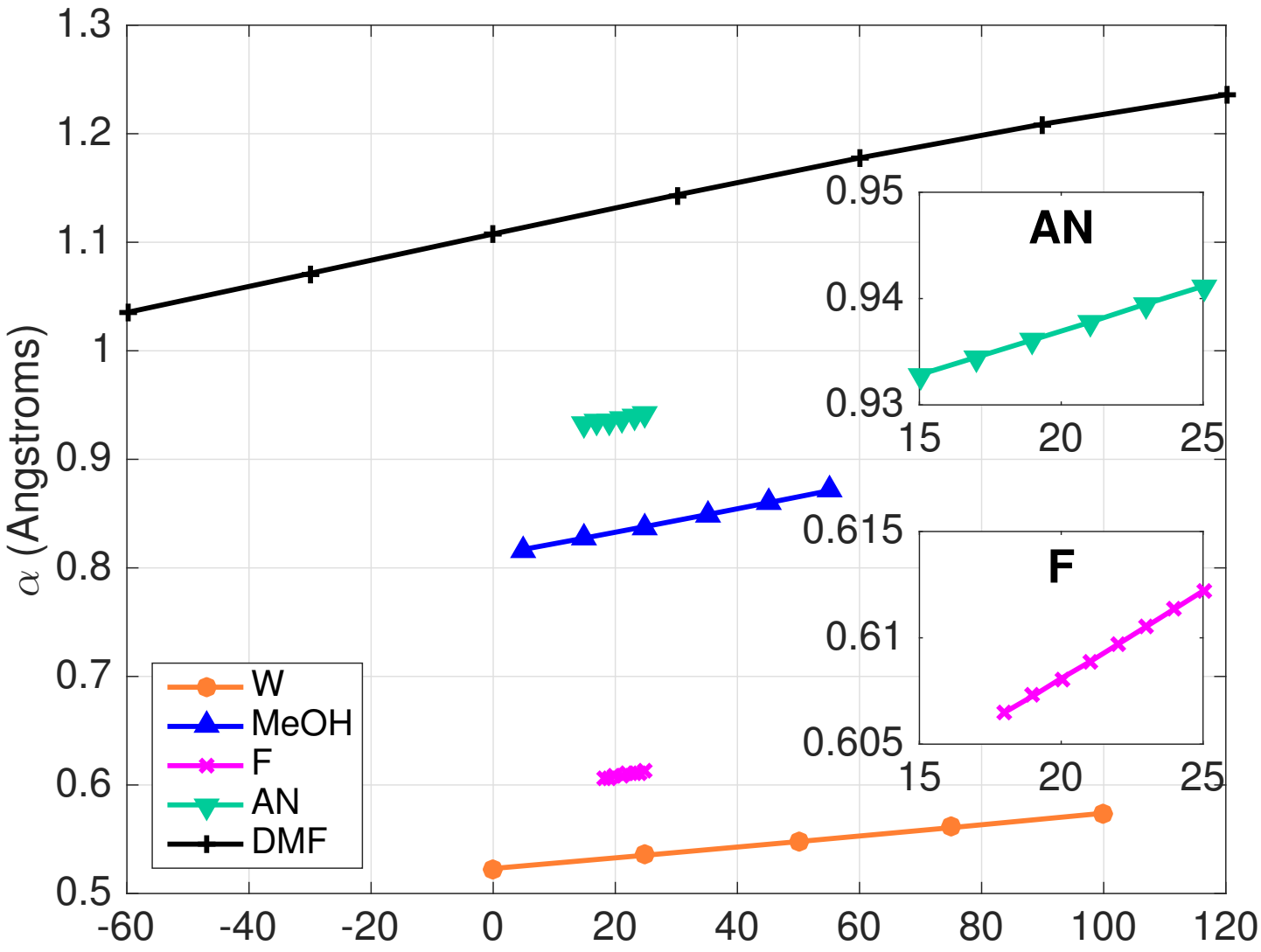
Accuracy of SLIC

Synthetic Molecules



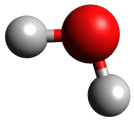
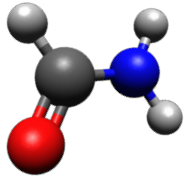
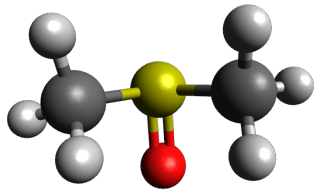
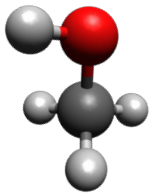
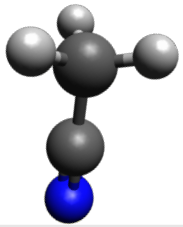
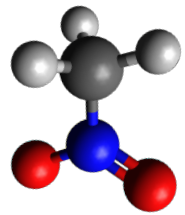
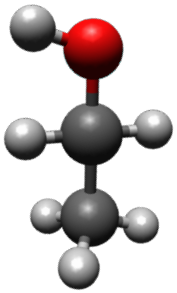
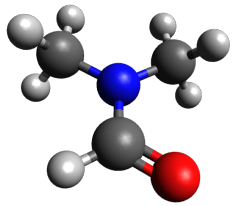
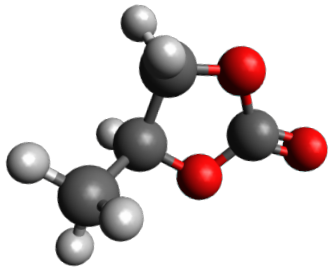
Thermodynamics

The parameters show linear temperature dependence



Model Validation

Courtesy A. Molvai Tabrizi

Water H_2O 	Formamide CH_3NO 	Dimethyl sulfoxide C_2H_6OS 
Methanol CH_3OH 	Acetonitrile C_2H_3N 	Nitromethane CH_3NO_2 
Ethanol C_2H_5OH 	Dimethyl formamide C_3H_7NO 	Propylene carbonate $CH_3C_2H_3O_2CO$ 

Model Validation

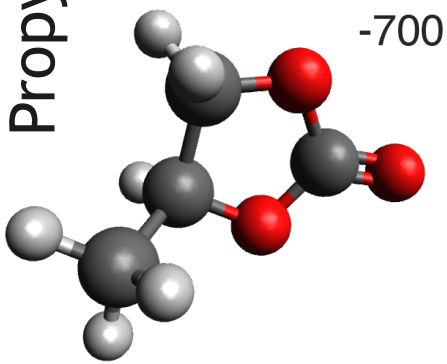
Courtesy A. Molvai Tabrizi

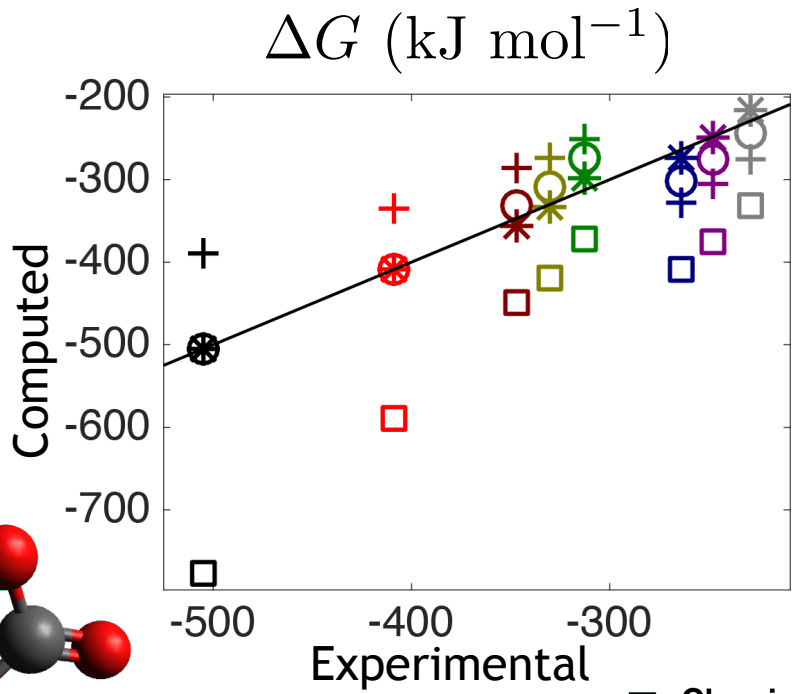
Solvent	r_s (Å)	$\epsilon_{out}(T)$	$\epsilon_{out}(25°C)$
W	1.370	$\epsilon_{out} = 87.740 - 4.0008\text{e}{-1}\ T + 9.398\text{e}{-4}\ T^2 - 1.410\text{e}{-6}\ T^3$	78.3
MeOH	1.855	$\log_{10}\epsilon_{out} = \log_{10}(32.63) - 2.64\text{e}{-3}(T - 25)$	32.6
EtOH	2.180	$\log_{10}\epsilon_{out} = \log_{10}(24.30) - 02.70\text{e}{-3}\ (T - 25)$	24.3
F	1.725	$\epsilon_{out} = 109 - 7.2\text{e}{-1}\ (T - 20)$	105.4
AN	2.135	$\epsilon_{out} = 37.50 - 1.6\text{e}{-1}\ (T - 20)$	36.7
DMF	2.585	$\epsilon_{out} = 42.04569 - 2.204448\text{e}{-1}\ T + 7.718531\text{e}{-4}\ T^2 - 1.000389\text{e}{-6}\ T^3$	37.0
DMSO	2.455	$\epsilon_{out} = -60.5 + (5.7\text{e}4/(T + 273.15)) - (7.5\text{e}6/(T + 273.15)^2)$	46.3
NM	2.155	$\log_{10}\epsilon_{out} = \log_{10}(35.8) - 1.89\text{e}{-3}\ (T - 30)$	36.6
PC	2.680	$\epsilon_{out} = 56.670738 + 2.58431\text{e}{-1}\ T - 7.7143\text{e}{-4}\ T^2$	62.6

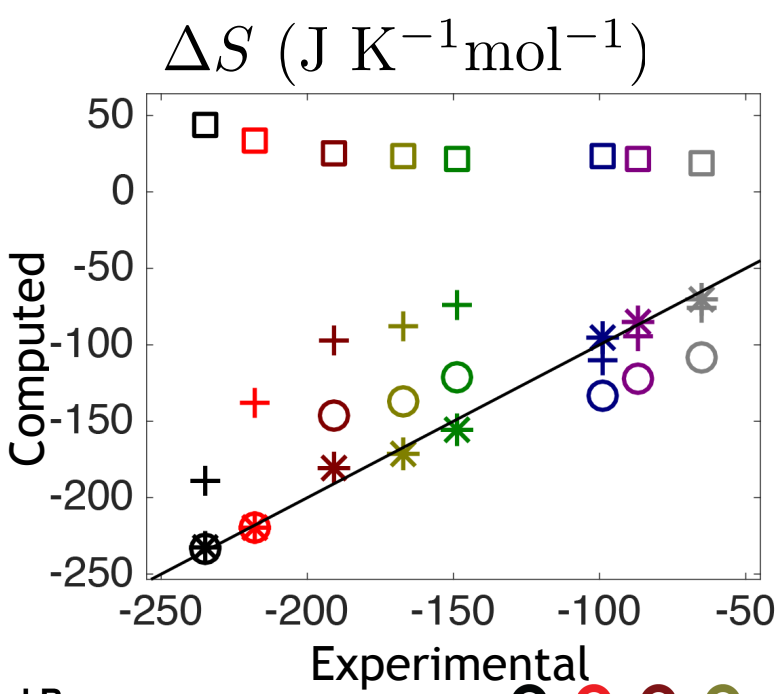
Model Validation

Courtesy A. Molvai Tabrizi

Propylene carbonate
$CH_3C_2H_3O_2CO$





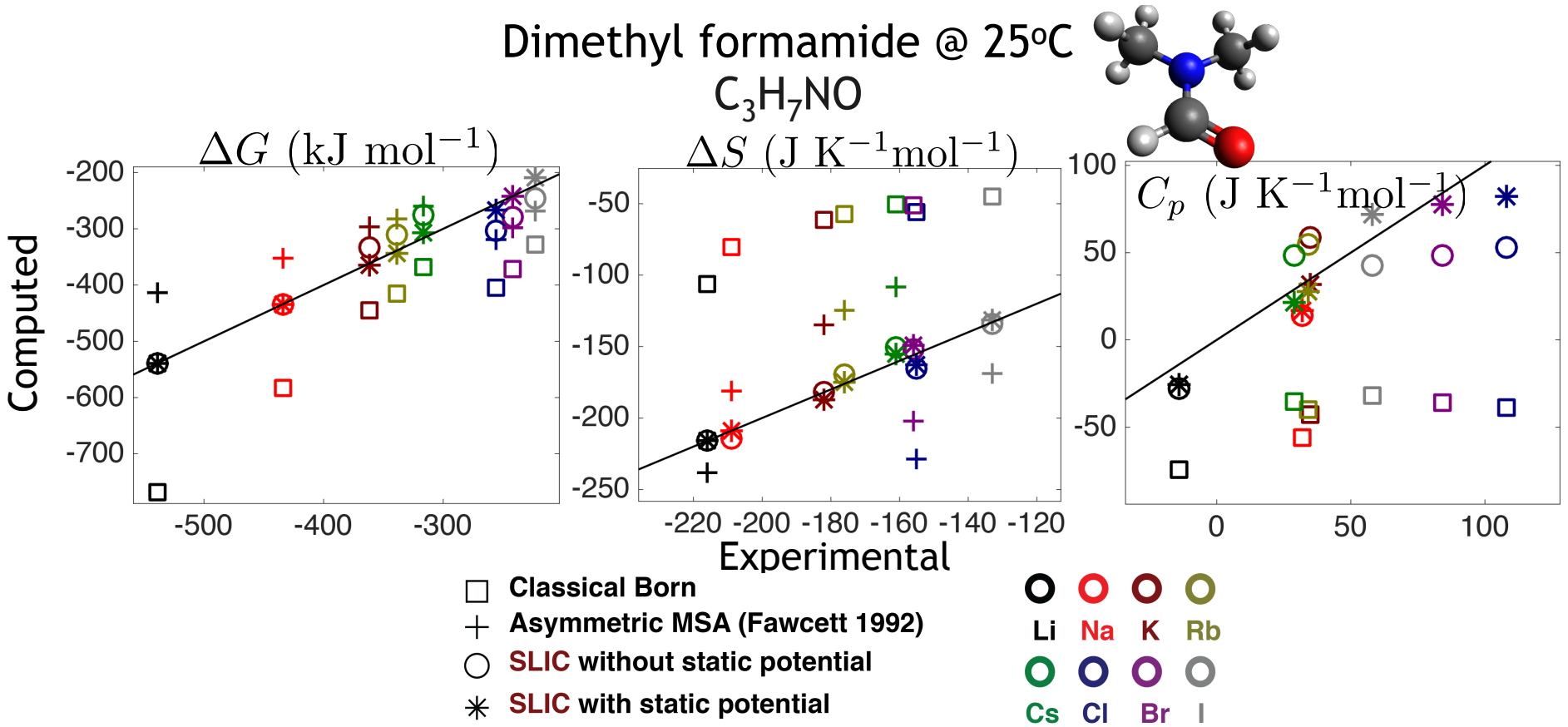


- Classical Born
- Asymmetric MSA (Fawcett 1992)
- SLIC without static potential
- SLIC with static potential

Li Na K Rb
Cs Cl Br I

Model Validation

Courtesy A. Molvai Tabrizi



Model Validation

Courtesy A. Molvai Tabrizi

A. Molavi Tabrizi, M.G. Knepley, and J.P. Bardhan, *Generalising the mean spherical approximation as a multiscale, nonlinear boundary condition at the solute-solvent interface*, Molecular Physics (2016).

Thermodynamic Predictions

Courtesy A. Molvai Tabrizi

Solvent	Ion	ΔG (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})	C_p (J K^{-1} mol^{-1})
W	F^-	-430 (-429)	-67 (-115)	-86 (-45)
MeOH	Rb^+	-326(-319)	-178 (-175)	55
	F^-	-415	-116	-79 (-131)
EtOH	Rb^+	-319 (-313)	-197 (-187)	128
	F^-	-405	-145	-153 (-194)
F	Rb^+	-340 (-334)	-135 (-130)	27
	F^-	-418	-128	36 (28)
AN	F^-	-390	-192	147
DMF	F^-	-389	-230	105
DMSO	Rb^+	-348 (-339)	-151 (-180)	32
	F^-	-400	-160	186(60)
NM	Rb^+	-324 (-318)	-186 (-183)	19
	F^-	-391	-182	95(71)
PC	F^-	-394	-149	67

Experimental Data in Parentheses

Thermodynamic Predictions

Courtesy A. Molvai Tabrizi

A. Molavi Tabrizi, S. Goossens, A.M. Rahimi, M.G. Knepley, and J.P. Bardhan, *Predicting Solvation Free Energies and Thermodynamics in Polar Solvents and Mixtures Using a Solvation-Layer Interface Condition (SLIC).* Journal of Chemical Physics (2017).

Thank You!

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