Fast estimation of ion-pairing for screening battery electrolytes

Ajay Muralidharan & Arun Yethiraj
Chemistry Department, University of Wisconsin Madison

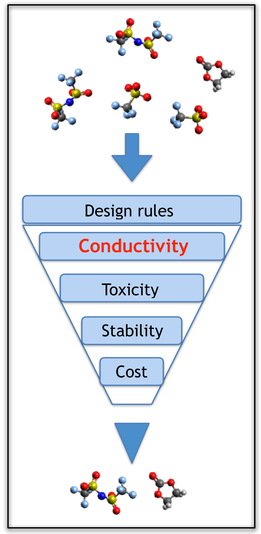
Introduction

Goal: To develop robust and fast methods to predict molecular properties for computational screening of battery electrolytes.

An important performance metric is the conductivity of the working ion (e.g. Li^+ in lithium ion battery).

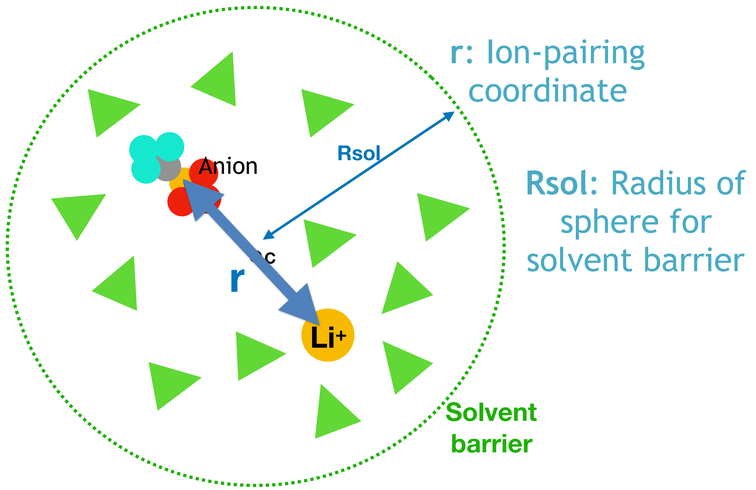
Weak ion-pairing between Li^+ and anion typically leads to better conductivity and performance.

We created a novel simulation tool (ClusterMT) that evaluates ion-pairing metrics efficiently and accurately.



Screening criteria for battery electrolytes

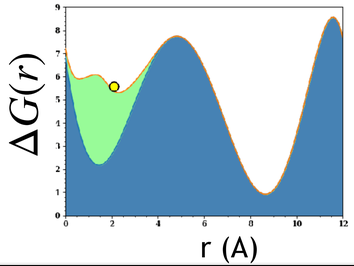
ClusterMT tool



Ion-pairing: Can a molecular cluster approximate bulk properties?

- Considers a cluster of size Rsol with a solvent barrier.
- Avoids outer shell solvents beyond Rsol. (reduces complexity)
- On-the-fly Probability Enhanced Sampling (OPES) [1] accelerates exploration of local conformations. (increases efficiency)

Theory: *On-the-fly Probability Enhanced Sampling (OPES)[1]*



"Add Gaussian bias/Hills"

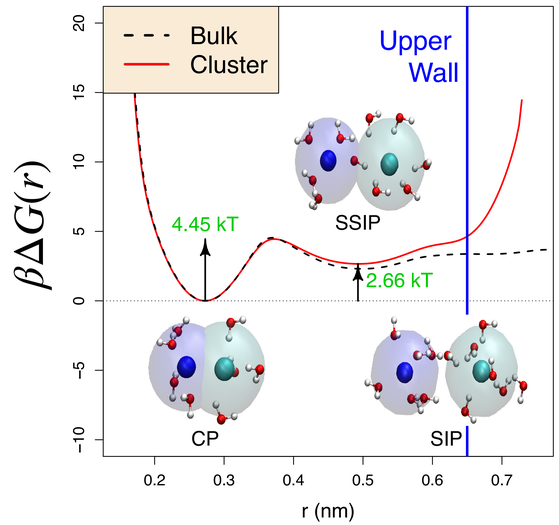
$$V_{opes} = \Sigma_n (1 - \frac{1}{\gamma}) \frac{1}{\beta} log(\frac{P_n(r)}{Z_n})$$

$$V_T(r) = V_{opes} + V_{\text{wall}} + V_{\text{solv.barrier}}$$ "Total bias (B)"

$$\langle r \rangle_0 = \frac{\left\langle r\, e^{\beta V_T} \right\rangle_B}{\left\langle e^{\beta V_T} \right\rangle_B}$$ "Reweight bias"

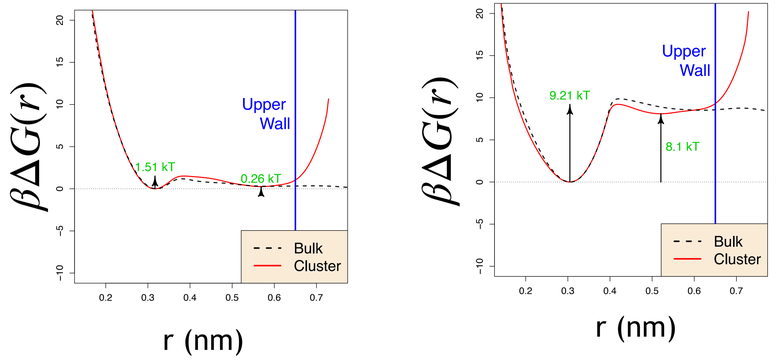
$$\beta\, \Delta G(r) = -\ln P(r)$$ "Free energy"

Test case: Sodium chloride (H_2O)



Accurate & fast (2 orders of magnitude efficiency gain compared to previous bulk calculations: 5 minutes per anion)

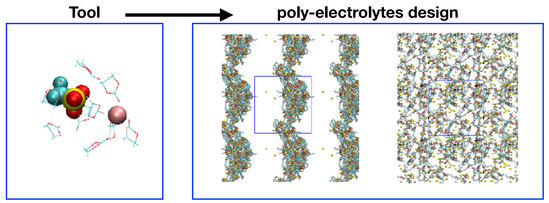
Results



Free energy along Li^+—anion coordinate. TFSI anion (Left panel) displays weak binding compared to OTF anion. OTF will be screened out. Note that Cluster calculations are in excellent agreement with bulk calculations [2].

Conclusion & Future directions

- Cluster model with enhanced sampling is potentially a great tool for screening novel high performance battery electrolytes.
- For polyelectrolytes design, properties can be controlled by tuning interactions between monomer species and counter-ion.
- Dissociation barrier data can be obtained for a library of chemical species and group contributions can potentially be "machine learnt" based on informatics tools.



Utility in polyelectrolyte design

References

1. M. Invernizzi et al., (2020). The Journal of Physical Chemistry Letters 11, 2731-2736.
2. A. Muralidharan et al., (2021). The Journal of Physical Chemistry B 125 (17), 4447-4455.

This research was partially funded by Hirschfelder fellowship funding and DOE (DE-SC0017877). Computational support from Center For High Throughput Computing (CHTC), UW-Madison

amuralidhar4@wisc.edu