



A general model for the electrochemical double layer in solids

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Computational Catalysis (DFT)

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Continuum-Scale Battery Modeling

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DFT / Cluster Expansions

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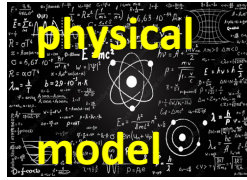


NASA's X-57 "Maxwell" all-electric aircraft



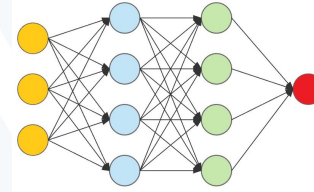
NASA partner Joby aviation tests components at an Ames wind tunnel

inputs



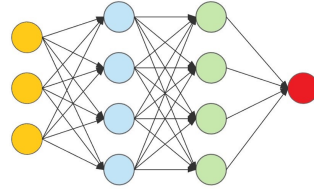
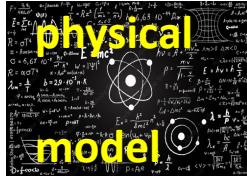
inaccurate
outputs

inputs



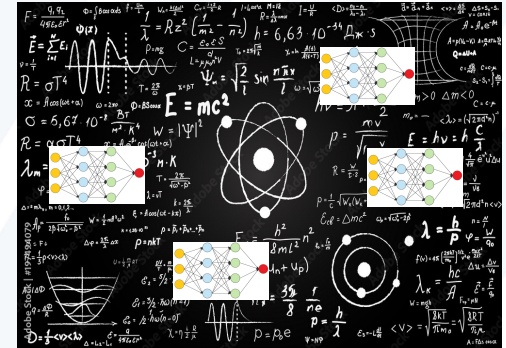
uninterpret-
able outputs

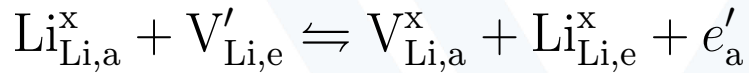
inputs



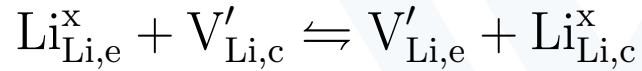
still cant
extrapolate

embedded machine learning

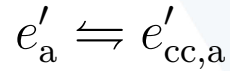




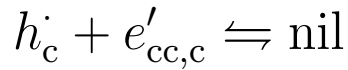
anode-electrolyte



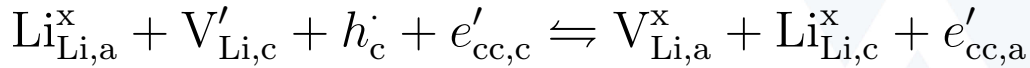
cathode-electrolyte



anode-CC



cathode-CC



overall cell



$$\zeta_{\text{h}} = \zeta_{\text{vc}}$$

$$\text{SOC} = f_{\text{c}}(\zeta_{\text{vc}}) = f_{\text{a}}(\zeta_{\text{va}})$$

$$V = -\frac{\mu_{\text{ecc,c}} - \mu_{\text{ecc,a}}}{F} = \phi_{\text{cc,c}} - \phi_{\text{cc,a}} =$$

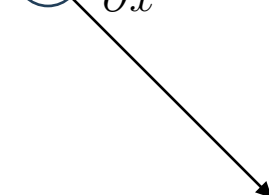
$$\underbrace{\frac{\mu_{\text{vc}}^0 + \mu_{\text{h}}^0 - \mu_{\text{va}}^0}{F} + \frac{RT}{F} \ln \left(\frac{\gamma_{\text{vc}} \gamma_{\text{h}}}{\gamma_{\text{va}}} \right)}_{\delta_{\text{SOC}}(\zeta_{\text{vc}}, T)} + \frac{RT}{F} \ln \left[\frac{\zeta_{\text{vc}} \zeta_{\text{h}} (1 - \zeta_{\text{va}})}{(1 - \zeta_{\text{vc}})(1 - \zeta_{\text{h}}) \zeta_{\text{va}}} \right]$$

transport / governing equations in the anode

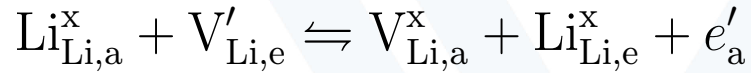
$$\mu_{\text{va}} = \mu_{\text{va}}^0 + RT \ln \gamma_{\text{va}} + RT \ln \left(\frac{\zeta_{\text{va}}}{1 - \zeta_{\text{va}}} \right)$$

$$f_{\text{va}} = -n_{\text{a}} \frac{\epsilon_{\text{a}}}{\tau_{\text{a}}} \zeta_{\text{va}} \overset{u_{\text{va}}}{\frac{\partial \mu_{\text{va}}}{\partial x}}$$

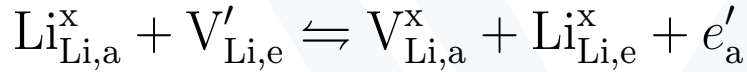
$$n_{\text{a}} \frac{\partial \zeta_{\text{va}}}{\partial t} = -\frac{\partial}{\partial x} f_{\text{va}}$$


$$\exp [\delta_{u_{\text{va}}}(\zeta_{\text{va}}, T)]$$

$$n_{\text{a}} \frac{\partial \zeta_{\text{va}}}{\partial t} = -\frac{\partial}{\partial x} f_{\text{va}} - r_{\epsilon, \text{a}} \frac{\partial \epsilon_{\text{a}}}{\partial t}$$



$$\kappa_{\text{ae}} = \exp \left[\underbrace{-\frac{\mu_{\text{va}}^0 + \mu_{\text{qa}}^0 - \mu_{\text{ve}}^0}{RT} - \frac{\gamma_{\text{va}}}{\gamma_{\text{ve}}}}_{\delta_{\kappa_{\text{ae}}}(\zeta_{\text{va}}, \zeta_{\text{ve}}, T)} \right] \exp \left(-\frac{F\Delta\phi_{\text{ae}}}{RT} \right) = \frac{\zeta_{\text{va}}(1 - \zeta_{\text{ve}})}{\zeta_{\text{ve}}(1 - \zeta_{\text{va}})}$$



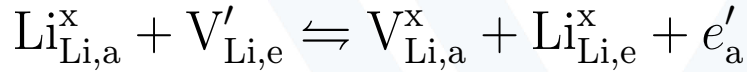
Butler-Volmer theory (refresher)

$$k_{\text{f}} = \xi \exp\left(\frac{\Delta S_{\text{f}}^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H_{\text{f}}^{\ddagger}}{RT}\right) \exp\left[-\alpha \frac{F \Delta \phi_{\text{ae}}}{RT}\right]$$

$$\kappa = k_{\text{f}}/k_{\text{b}} \longrightarrow k_{\text{b}} = \xi \exp\left(\frac{\Delta S_{\text{b}}^{\ddagger}}{R}\right) \exp\left(-\frac{\Delta H_{\text{b}}^{\ddagger}}{RT}\right) \exp\left[(1 - \alpha) \frac{F \Delta \phi_{\text{ae}}}{RT}\right]$$

$$r_{\text{ae}} = k_{\text{ae}}^{0*} \left\{ \exp\left[-\alpha \frac{F(\Delta \phi_{\text{ae}} - \Delta \phi_{\text{ae}}^0)}{RT}\right] - \exp\left[(1 - \alpha) \frac{F(\Delta \phi_{\text{ae}} - \Delta \phi_{\text{ae}}^0)}{RT}\right] \right\}$$

$$k_{\text{ae}}^{0*} = k_{\text{f}}^0 \zeta_{\text{ve}} (1 - \zeta_{\text{va}}) = k_{\text{b}}^0 \zeta_{\text{va}} (1 - \zeta_{\text{ve}})$$



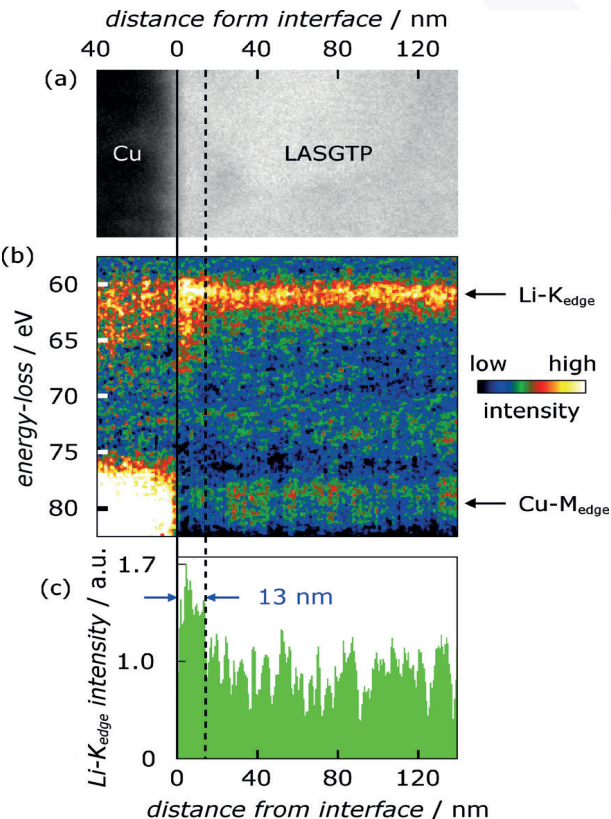
$$r_{\text{ae}} = k_{\text{ae}}^{0*} \left\{ \exp \left[-\alpha \frac{F(\Delta\phi_{\text{ae}} - \Delta\phi_{\text{ae}}^0)}{RT} \right] - \exp \left[(1 - \alpha) \frac{F(\Delta\phi_{\text{ae}} - \Delta\phi_{\text{ae}}^0)}{RT} \right] \right\}$$

$$k_{\text{ae}}^{0*} = k_{\text{f}}^0 \zeta_{\text{ve}} (1 - \zeta_{\text{va}}) = k_{\text{b}}^0 \zeta_{\text{va}} (1 - \zeta_{\text{ve}})$$

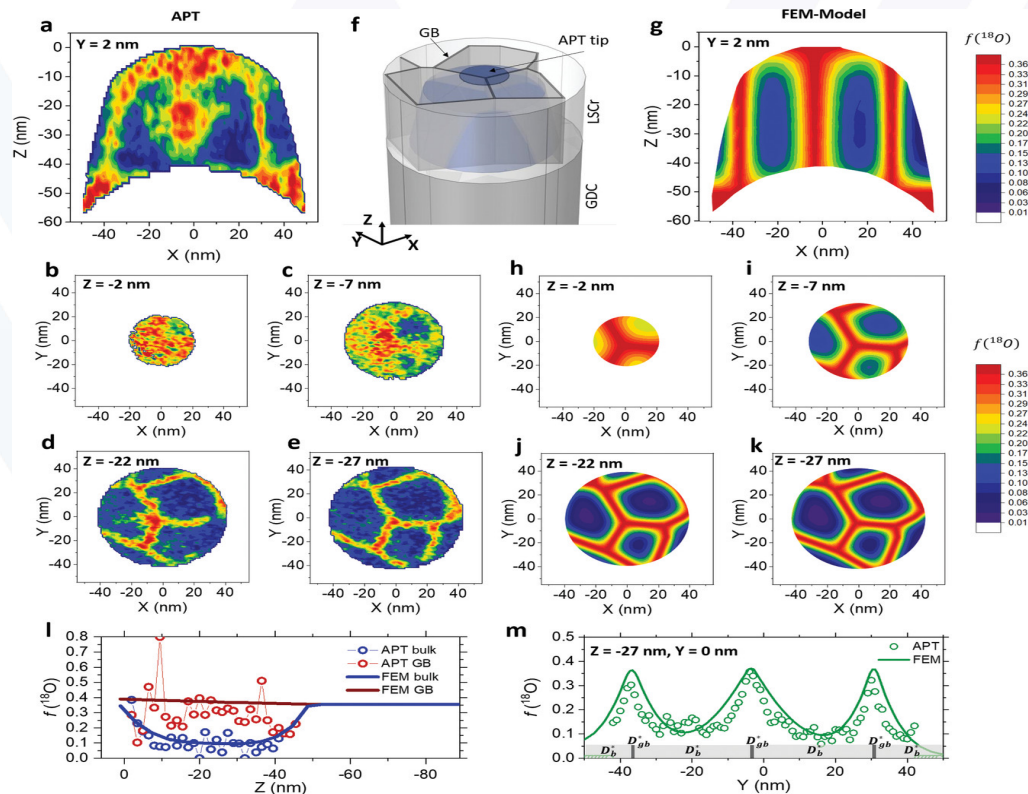
$$k_{\text{f}}^0 \exp \left[-\alpha \frac{F\eta_{\text{ae}}}{RT} \right] = \exp \left[\delta_{k_{\text{ae}}}(\zeta_{\text{ve}}, \zeta_{\text{va}}, \eta_{\text{ae}}, T) \right] \quad \eta_{\text{ae}} = \Delta\phi_{\text{ae}} - \Delta\phi_{\text{ae}}^0$$

$$\Rightarrow r_{\text{ae}} = k_{\text{ae}}^0 \left[1 - \exp \left(\frac{F\eta_{\text{ae}}}{RT} \right) \right]$$

$$k_{\text{ae}}^0 = \exp \left[\delta_{k_{\text{ae}}}(\zeta_{\text{ve}}, \zeta_{\text{va}}, \eta_{\text{ae}}, T) \right] \zeta_{\text{ve}} (1 - \zeta_{\text{va}})$$

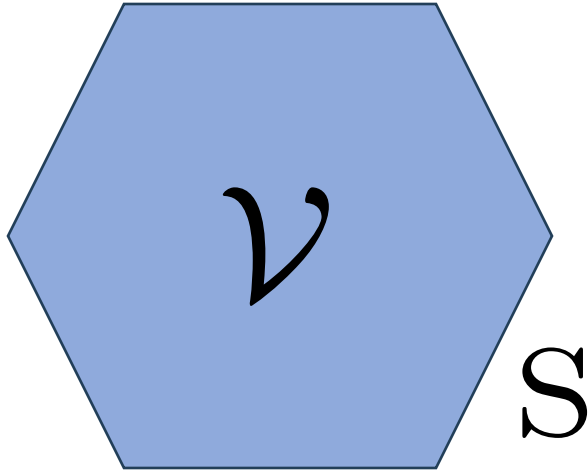


Y. Nomura, *et al.*, *Angew. Chem.* **58** (2019) 5292.



F. Baiutti, *et al.*, *Advanced Materials*, 2021

$$\mathcal{F} = \mathcal{F}_S(\zeta_S) + n \int_V \left\{ \mathcal{F}_0(\mathbf{x}, \zeta, \{|\nabla \zeta_j|^2\}, T) + RT \sum_j [\zeta_j \ln \zeta_j + (1 - \zeta_j) \ln (1 - \zeta_j)] \right. \\ \left. + \mathcal{F}_x(\zeta, T) + F \sum_j z_j \zeta_j \phi - \frac{1}{2n} \epsilon_r \epsilon_0 |\nabla \phi|^2 \right\}$$



$\mathcal{F}_0$ → excess molar free energy due to the presence of the interface

$\zeta = \{\zeta_j\}$ → site fractions of lattice defects

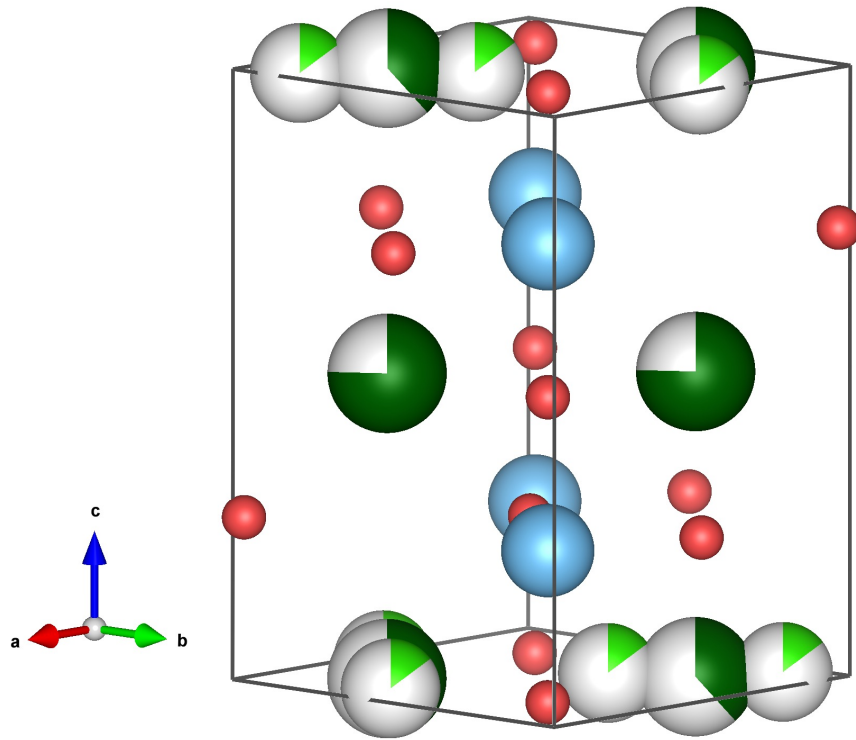
$\mathcal{F}_x$ → bulk excess molar free energy

n → density of formula units

$$\begin{aligned}
 \delta \mathcal{F} = & \delta \mathcal{F}_S + n \sum_j \int_V \left[\frac{\partial \mathcal{F}_0}{\partial \zeta_j} + RT \ln \left(\frac{\zeta_j}{1 - \zeta_j} \right) + \frac{\partial \mathcal{F}_x}{\partial \zeta_j} - 2 \frac{\partial \mathcal{F}_0}{\partial |\nabla \zeta_j|^2} \nabla^2 \zeta_j + z_j F \phi \right] \delta \zeta_j \\
 & + n \int_V \left[F \sum_j z_j \zeta_j + \frac{1}{n} \epsilon_r \epsilon_0 \nabla^2 \phi \right] \delta \phi \\
 & + 2n \sum_j \oint_S \frac{\partial \mathcal{F}_0}{\partial |\nabla \zeta_j|^2} \nabla \zeta_j \cdot \hat{n} \delta \zeta_j - \epsilon_r \epsilon_0 \oint_S \nabla \phi \cdot \hat{n} \delta \phi
 \end{aligned}$$

$$\mu_{x,j} = \frac{\partial \mathcal{F}_x}{\partial \zeta_j} + RT \ln \left(\frac{\zeta_j}{1 - \zeta_j} \right) \rightarrow \text{bulk chemical potential, calculable via DFT-based grand canonical Monte Carlo}$$

Once we have $\mathcal{F}_x$ is there a gcMC route to $\mathcal{F}_0$?



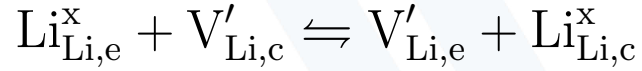
$\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3$ crystal structure
showing the displacement of
the Li atom

-15 meV difference compared
with the regular A-site

— difference for the NN pair

transport / governing equations in the electrolyte

$$f_{\text{ve}} = -\sigma_{\text{ve}} \frac{\partial \phi_{\text{e}}}{\partial x}$$
$$\frac{\partial^2 \phi_{\text{e}}}{\partial x^2} = 0$$



$$\kappa_{\text{ce}} = \exp \left[\underbrace{-\frac{\mu_{\text{ve}}^0 - \mu_{\text{vc}}^0}{RT} - \frac{\gamma_{\text{ve}}}{\gamma_{\text{vc}}}}_{\delta_{\kappa_{\text{ce}}}(\zeta_{\text{vc}}, \zeta_{\text{ve}}, T)} \right] \exp \left(-\frac{F\Delta\phi_{\text{ce}}}{RT} \right) = \frac{\zeta_{\text{ve}}(1 - \zeta_{\text{vc}})}{\zeta_{\text{vc}}(1 - \zeta_{\text{ve}})}$$

$$r_{\text{ce}} = k_{\text{ce}}^0 \left[1 - \exp \left(\frac{F\eta_{\text{ce}}}{RT} \right) \right]$$

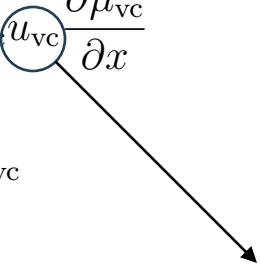
$$k_{\text{ce}}^0 = \exp \left[\delta_{k_{\text{ce}}}(\zeta_{\text{vc}}, \zeta_{\text{ve}}, \eta_{\text{ce}}, T) \right] \zeta_{\text{vc}}(1 - \zeta_{\text{ve}})$$

transport / governing equations in the cathode

$$\mu_{\text{vc}} = \mu_{\text{vc}}^0 + RT \ln \gamma_{\text{vc}} + RT \ln \left(\frac{\zeta_{\text{vc}}}{1 - \zeta_{\text{vc}}} \right) - F\phi_{\text{c}}$$

$$f_{\text{vc}} = -n_{\text{c}} \zeta_{\text{vc}} \left(u_{\text{vc}} \frac{\partial \mu_{\text{vc}}}{\partial x} \right)$$

$$n_{\text{c}} \frac{\partial \zeta_{\text{vc}}}{\partial t} = - \frac{\partial}{\partial x} f_{\text{vc}}$$


$$\exp [\delta_{u_{\text{vc}}}(\zeta_{\text{vc}}, T)]$$

$$\mu_j = \frac{\partial \mathcal{F}_0}{\partial \zeta_j} + RT \ln \left(\frac{\zeta_j}{1 - \zeta_j} \right) + \frac{\partial \mathcal{F}_x}{\partial \zeta_j} - 2 \frac{\partial \mathcal{F}_0}{\partial |\nabla \zeta_j|^2} \nabla^2 \zeta_j + z_j F \phi$$

$$\eta_j = -n u_j \zeta_j \nabla \mu_j$$

$u_j \rightarrow$ mobility, calculable via MD / kMC?

$$\frac{\partial \zeta_j}{\partial t} = \nabla \cdot (u_j \zeta_j \nabla \mu_j)$$