Nissan Leaf

Electrochemistry simulations using ONETEP

Arihant Bhandari, Chao Peng, Jacek Dziedzic, Lucian Anton, John R. Owen, Denis Kramer, Chris-Kriton Skylaris

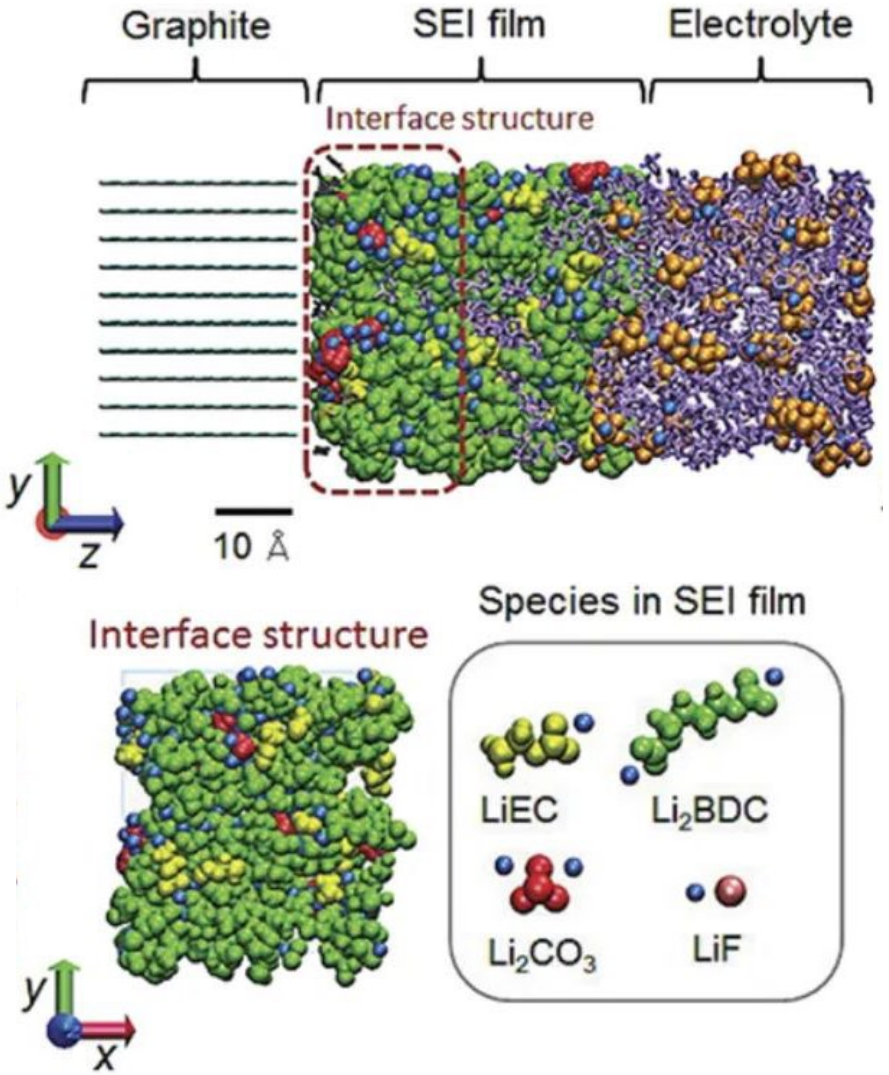
University of Southampton, United Kingdom

THE FARADAY INSTITUTION Modelling

MULTI-SCALE MODELLING

Simulations of Solid-Electrolyte Interfaces

- Explicit Solvation
  - Treats all species at the same level of chemical accuracy:
    - Electrode (graphite)
    - Solvent (EC)
    - Electrolyte ($LiPF_6$)
    - SEI species (LiEC, Li_2CO_3, LiF, etc.)
  - Requires explicit structural details.
  - Requires statistical averaging over all possible configurations of all species.
  - Computationally costly.



Norio Takenaka; Yuichi Suzuki; Hirofumi Sakai; Masataka Nagaoka; *J. Phys. Chem. C* 2014, 118, 10874-10882.

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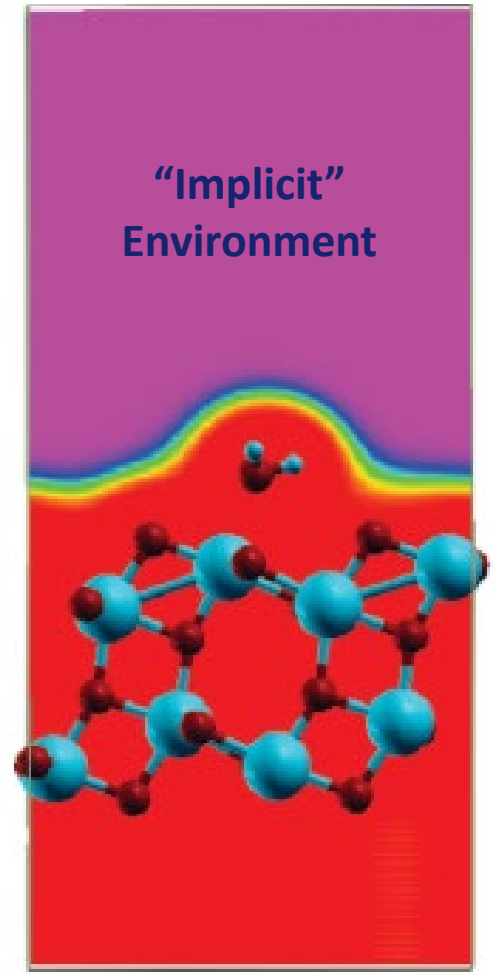
Simulations of Solid-Electrolyte Interfaces

Hybrid Quantum-Continuum Model

- Divides the system into two subsystems:
  - "Explicit" system which is treated quantum-mechanically,
  - In an "implicit" environment which is treated at a mean-field continuum level
- Automatically averages out degrees of freedom of environment.
- Computationally efficient.
- Focus on the explicit system.



Sánchez, V. M.; De La Llave, E.; Scherlis, D. A. Langmuir 2011, 27 (6), 2411–2419.

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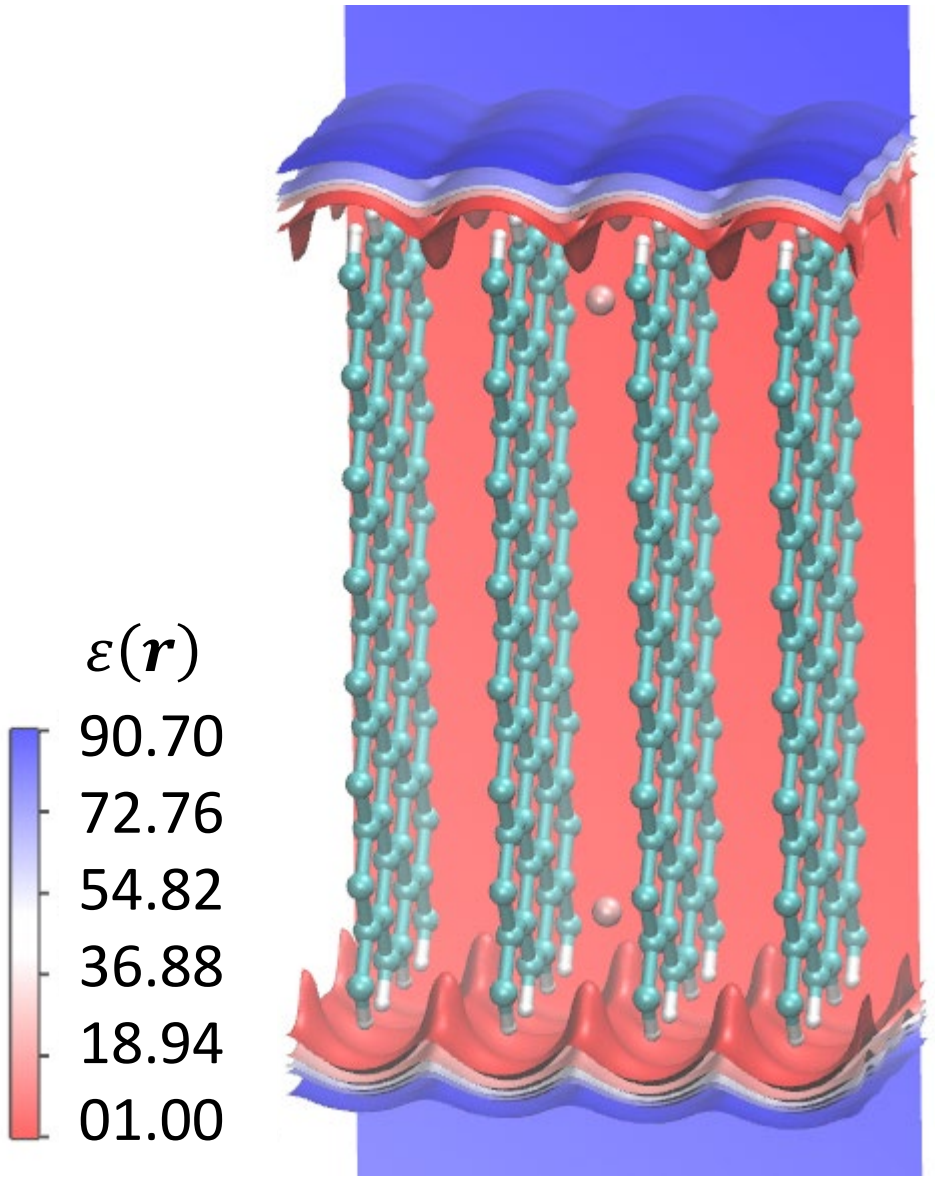
Implicit Model for Solvent

$$\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$$

- Dielectric continuum with smoothly varying permittivity
  - $\varepsilon(\boldsymbol{r}) = 1 + (\varepsilon_{\text{solvent}} - 1)\gamma(r)$
- Non-mean field contributions:
  - Cavitation
  - Solid-solvent dispersion
  - Solid-solvent repulsion

are also included as proportional to the solvent accessible surface area.



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- Non-mean field contributions:
  - Cavitation
  - Solid-solvent dispersion
  - Solid-solvent repulsion

are also included as proportional to the solvent accessible surface area.

Continuum Model for Mobile Electrolyte Ions

$$\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$$

- Electrolyte charge density

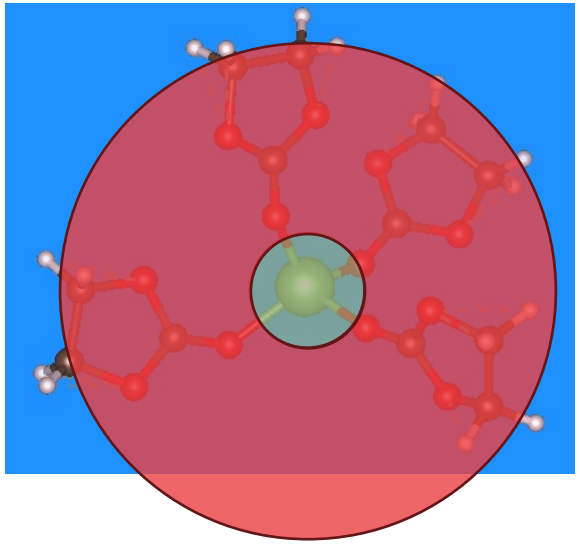
$$\rho_{mob}(\boldsymbol{r}) = \sum_i z_i c_i(\boldsymbol{r})$$

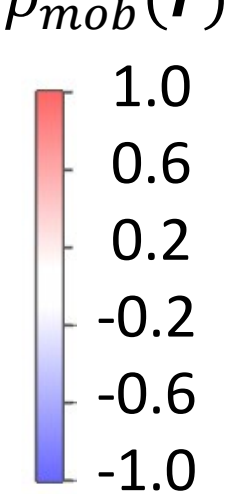
$$c_i(\boldsymbol{r}) = c^0 \lambda(\boldsymbol{r}) \exp\left(-\frac{z_i v(\boldsymbol{r})}{k_B T} + \frac{\mu_i}{k_B T}\right)$$

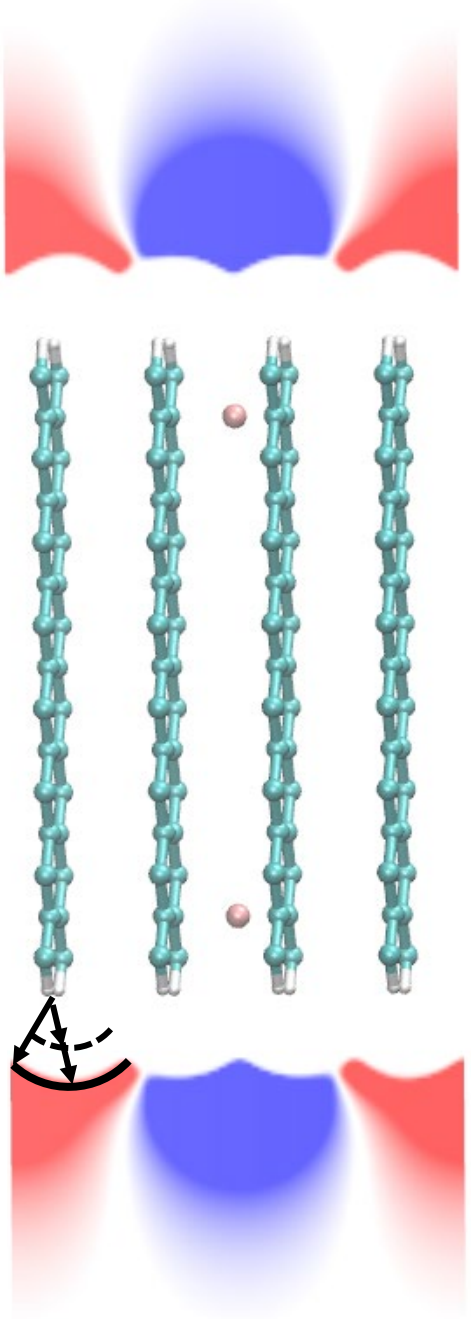
bulk values of electrolyte concentration

Solute size (ρ)

Solvation radius (R_s)







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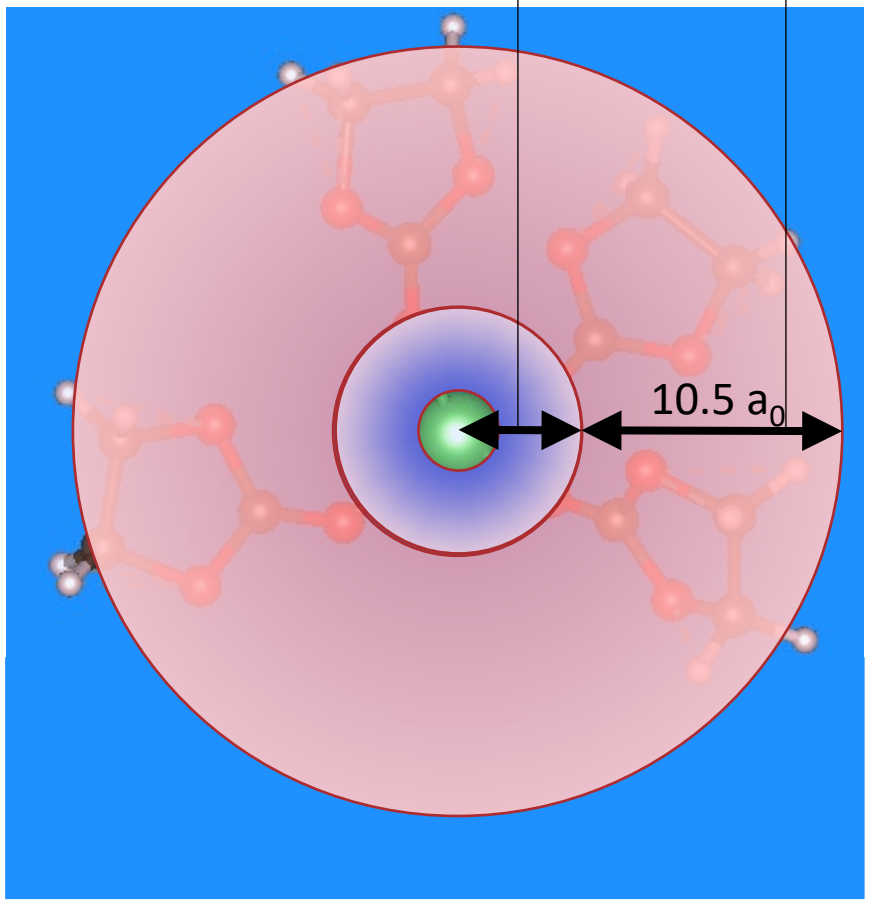
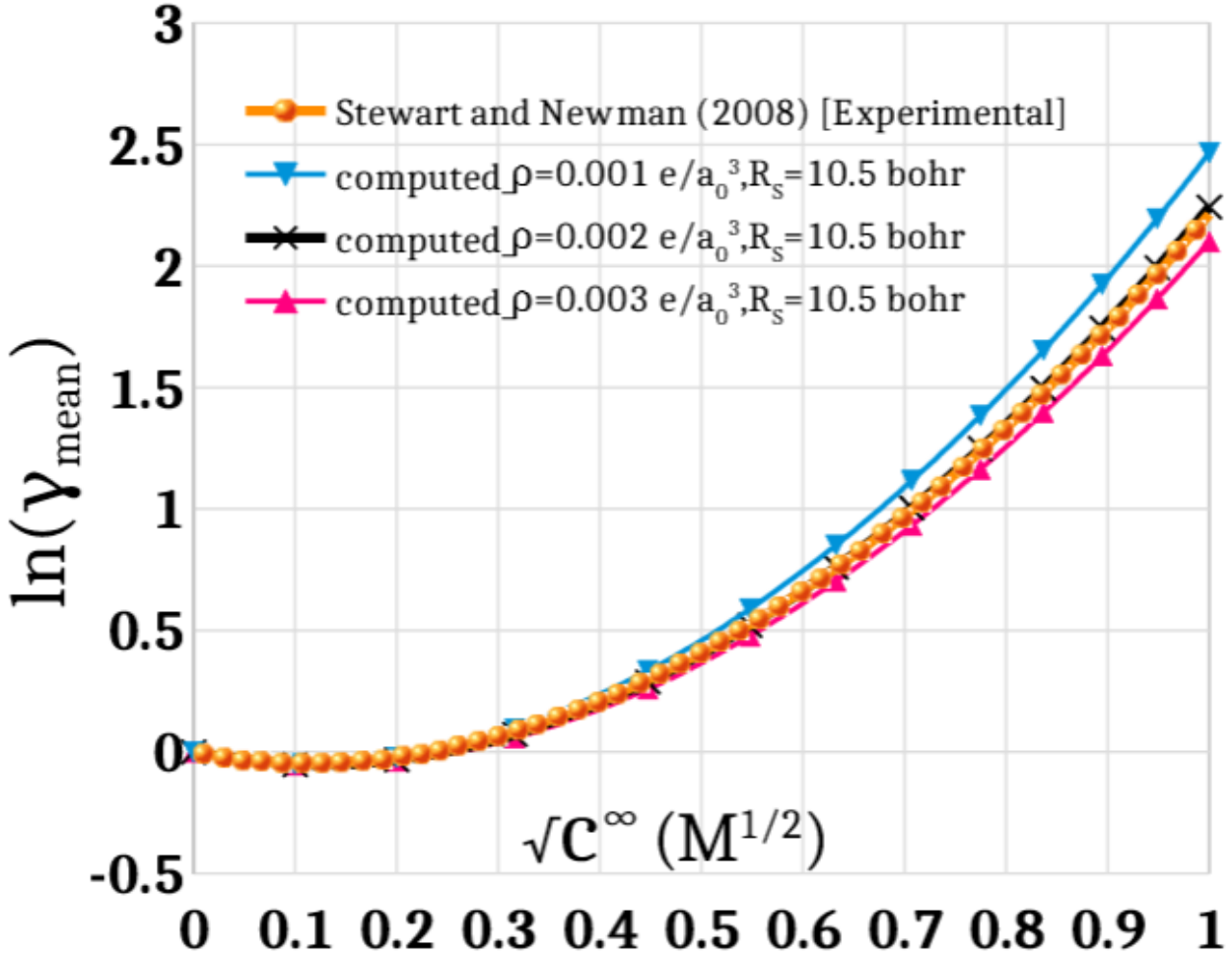
Electrolyte Parameters

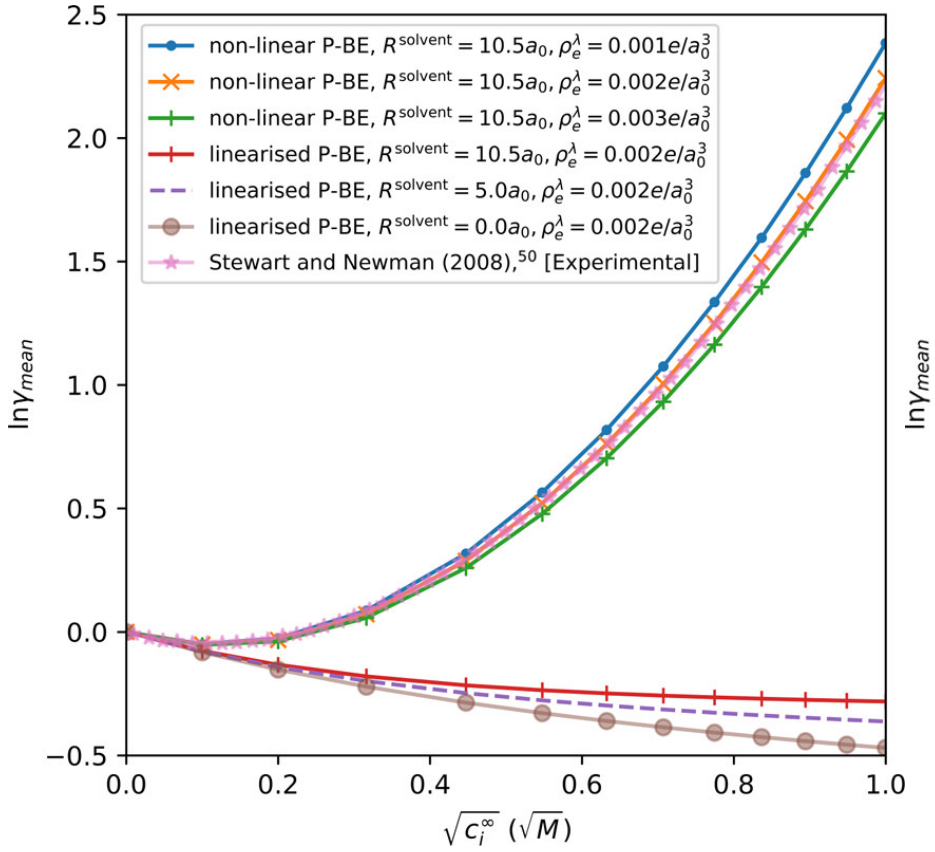
→ found by calibrating activity coefficients of electrolytes with experiments.

$$\lambda(\boldsymbol{r}) = \prod_{I}^{N} \frac{1}{2}\left[1 + \operatorname{erf}\left(\frac{|\boldsymbol{r} - \boldsymbol{R}_I| - R_{\text{solute}}(\rho) - R_{\text{solvent}}}{\sigma}\right)\right]$$

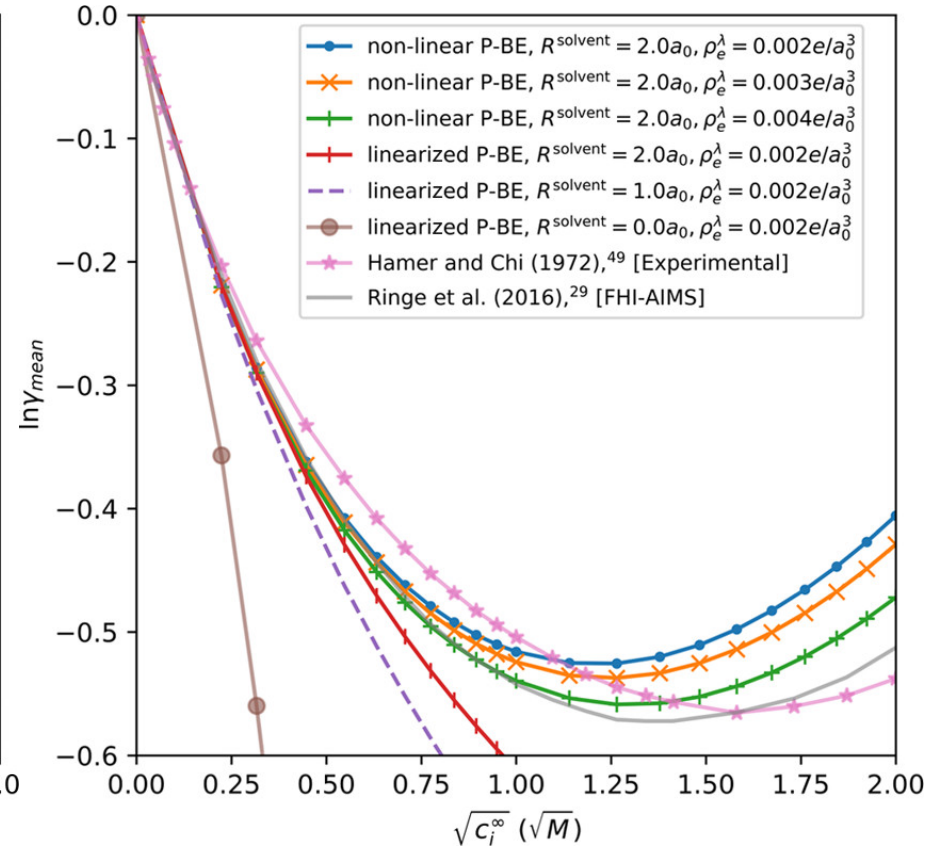




Electrolyte Parameters



$LiPF_6$ in EC at 308 K



KCl in water at 298 K

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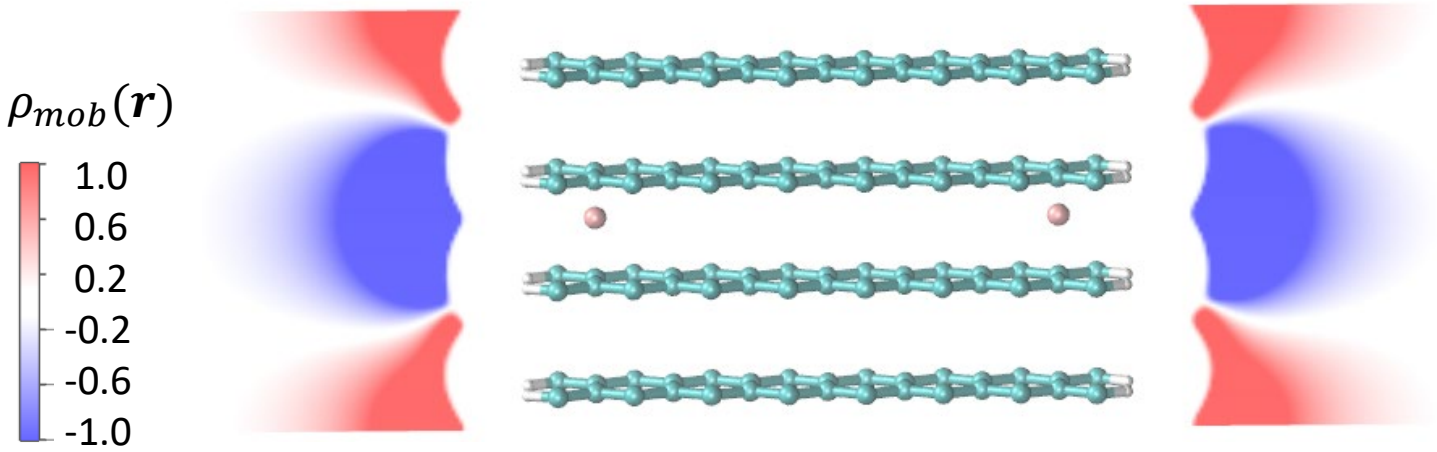
Practical Approach to Large-Scale Electronic Structure Calculations in Electrolyte Solutions via Continuum-Embedded Linear-Scaling Density Functional Theory

Jacek Dziedzic, Arihant Bhandari, Lucian Anton, Chao Peng, James C. Womack, Marjan Famili, Denis Kramer, and Chris-Kriton Skylaris*

Cite This: *J. Phys. Chem. C* 2020, 124, 7860−7872 Read Online

PBCs: Electroneutrality $\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$

Jellium	Accessible Jellium	Grand canonical electrolyte
Opposite background charge in the entire simulation cell.	Opposite background charge in the electrolyte accessible region.	Non-uniform background charge which follows Poisson-Boltzmann distribution and neutralizes the charge on atoms.
$\rho_{\mathrm{mob}}(\boldsymbol{r}) = -\frac{\int \rho(\boldsymbol{r}')d\boldsymbol{r}'}{\int d\boldsymbol{r}'}$	$\rho_{\mathrm{mob}}(\boldsymbol{r}) = -\frac{\lambda(\boldsymbol{r})\int \rho(\boldsymbol{r}')d\boldsymbol{r}'}{\int \lambda(\boldsymbol{r}')d\boldsymbol{r}'}$	$\rho_{\mathrm{mob}}(\boldsymbol{r}) = \lambda(\boldsymbol{r})\sum_{\boldsymbol{i}} z_i c_i^{\infty} \exp\left(\frac{-z_i[v(\boldsymbol{r}) + v_s]}{k_B T}\right)$



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The Journal of Chemical Physics

Electronic structure calculations in electrolyte solutions: Methods for neutralization of extended charged interfaces

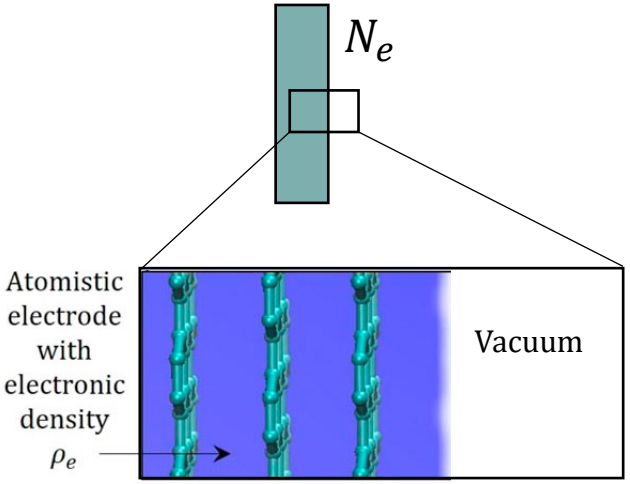
Cite as: J. Chem. Phys. 153, 124101 (2020); https://doi.org/10.1063/5.0021210
Submitted: 08 July 2020 . Accepted: 09 September 2020 . Published Online: 22 September 2020

Arihant Bhandari, Lucian Anton, Jacek Dziedzic, Chao Peng, Denis Kramer, and Chris-Kriton Skylaris

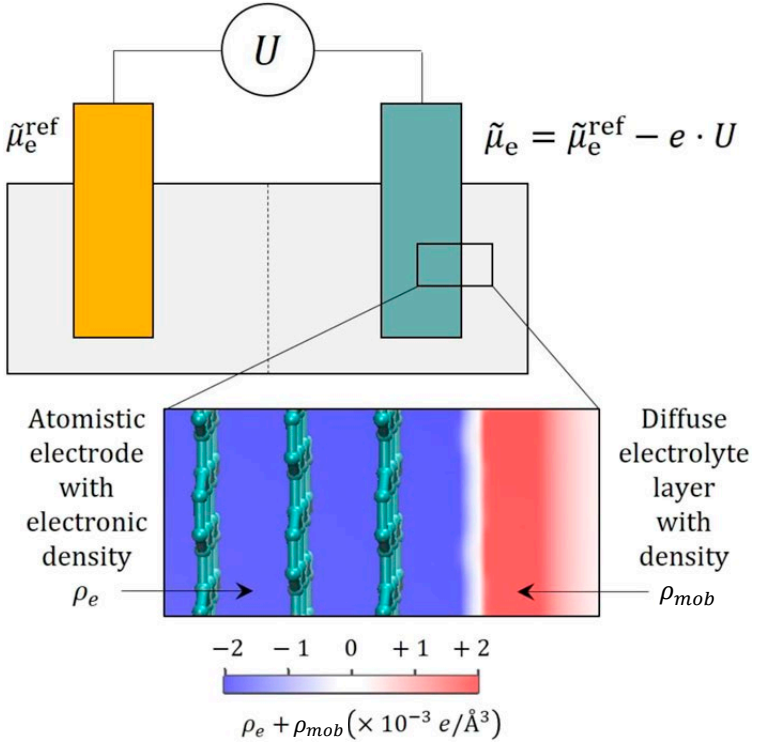
Grand canonical DFT for simulations of charged solid-liquid interfaces

Canonical ensemble of electrons

(constant number of electrons)



Grand canonical model for electrochemistry



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The Journal of Chemical Physics

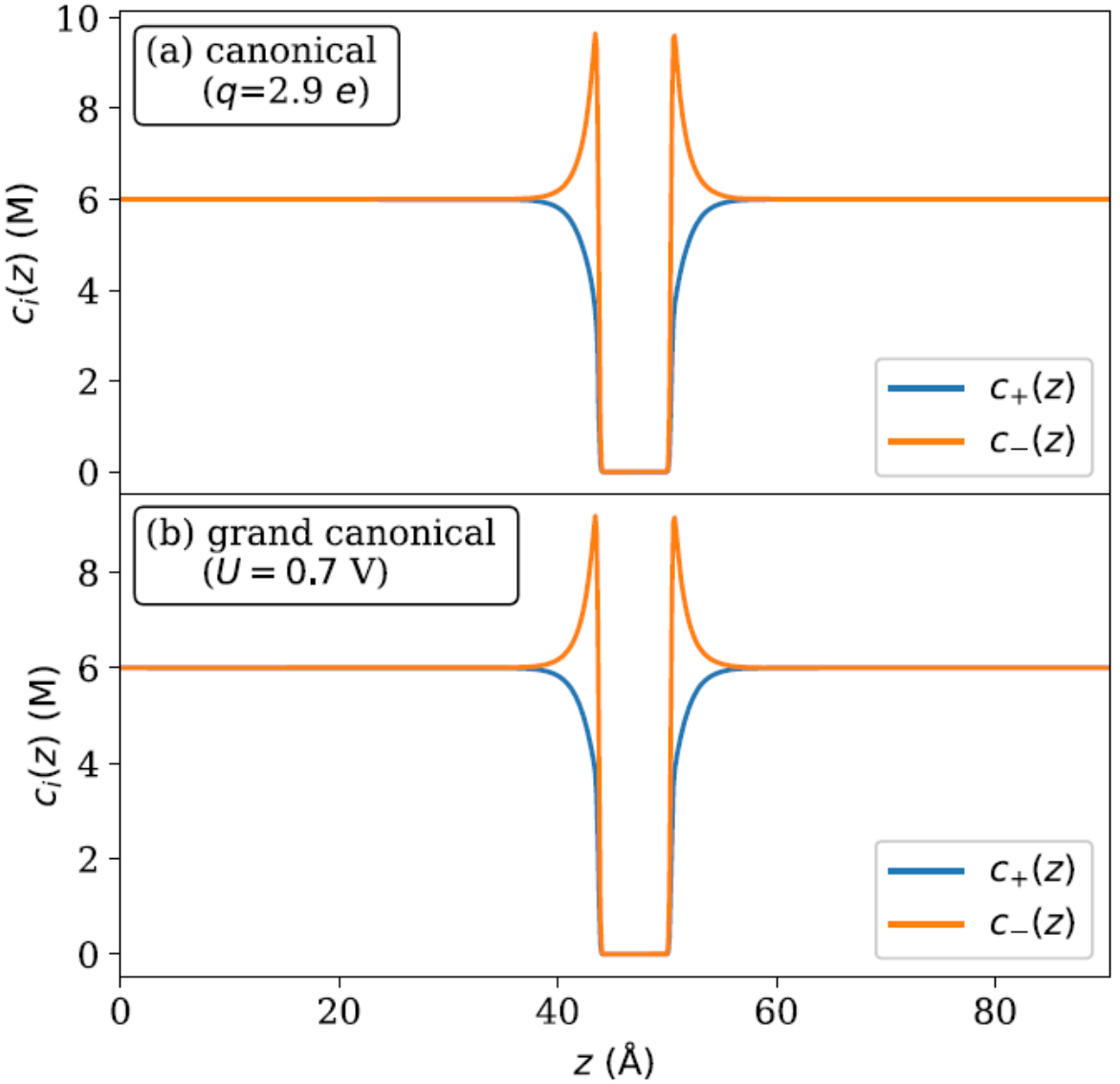
Electrochemistry from first-principles in the grand canonical ensemble

Cite as: J. Chem. Phys. **155**, 024114 (2021); https://doi.org/10.1063/5.0056514
Submitted: 11 May 2021 • Accepted: 22 June 2021 • Published Online: 12 July 2021

Arihant Bhandari, Chao Peng, Jacek Dziedzic, et al.

Ensemble for electrons

Canonical	Grand canonical
Electronically isolated system.	System connected with an electronic reservoir.
Number of electrons and the charge is fixed.	Chemical potential of electrons is fixed.
Chemical potential is found.	Charge is found.
$A = E - TS$	$\Omega = E - TS - \mu_e N_e$



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System

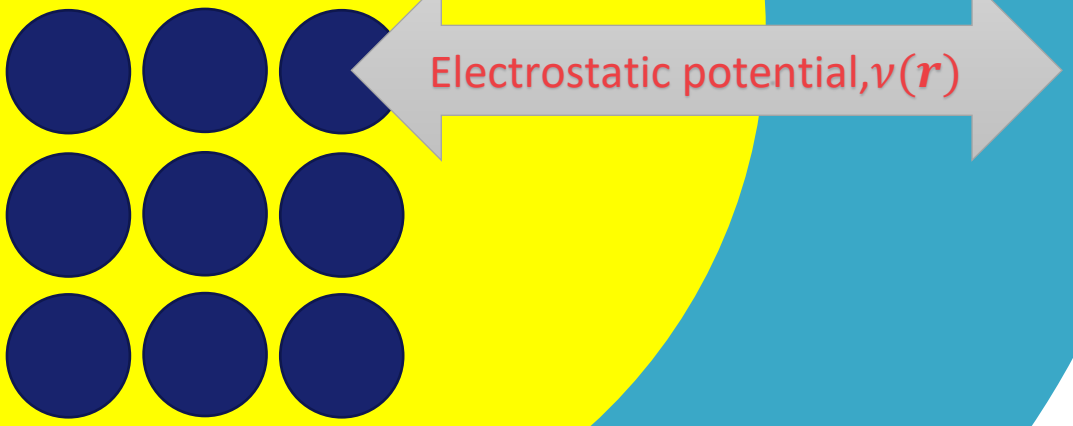
Dielectric solvent $\varepsilon(\boldsymbol{r})$
and
Continuum electrolyte

$z_i, c_i(\boldsymbol{r}), i = 1 \ldots p$

Quantum System

$\rho(\boldsymbol{r}) = \rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r})$

$\rho_e(\boldsymbol{r}) = \sum_k f_k \, \psi_k(\boldsymbol{r}) \psi_k^*(\boldsymbol{r})$



Electrostatic potential, $v(\boldsymbol{r})$

$$\Omega = \Omega_{\mathrm{e}}[\rho_{\mathrm{e}}]$$

$$+ \Omega_{\mathrm{mf}}[\rho_{\mathrm{e}}, v, c_i]$$

$$+ \Omega_{\mathrm{nmf}}$$

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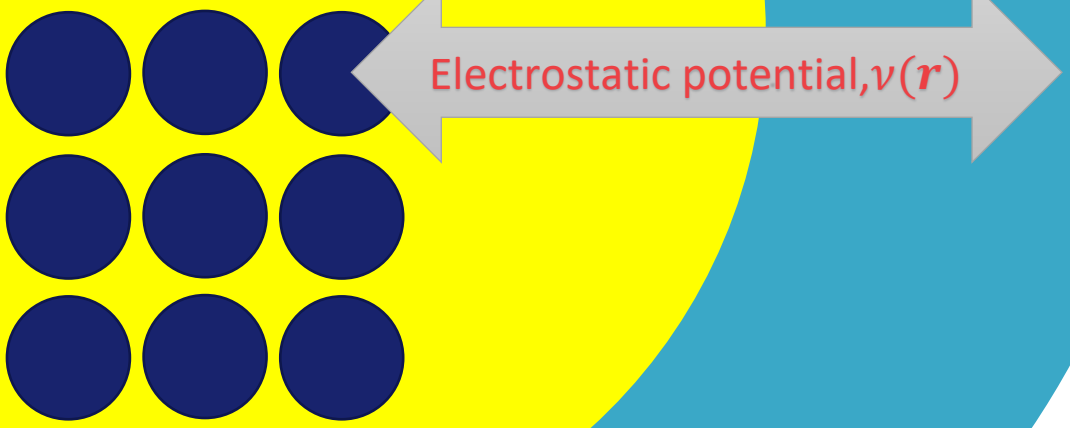

$$\Omega = \sum_k f_k \int \psi_k^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_k(\boldsymbol{r}) d\boldsymbol{r}$$ Kinetic energy

$$+k_B T \sum_k f_k \ln f_k + (1 - f_k) \ln f_k$$ Entropy

$$-\mu_{\mathrm{e}} \sum_k f_k$$ Chemical potential term

$$+\sum_k f_k \int \psi_k^*(\boldsymbol{r}) \, v_{\mathrm{ps}}(\boldsymbol{r}) \, \psi_k(\boldsymbol{r}) d\boldsymbol{r}$$ Pseudopotential contribution

$$+E_{\mathrm{xc}}$$ Exchange Correlation Energy

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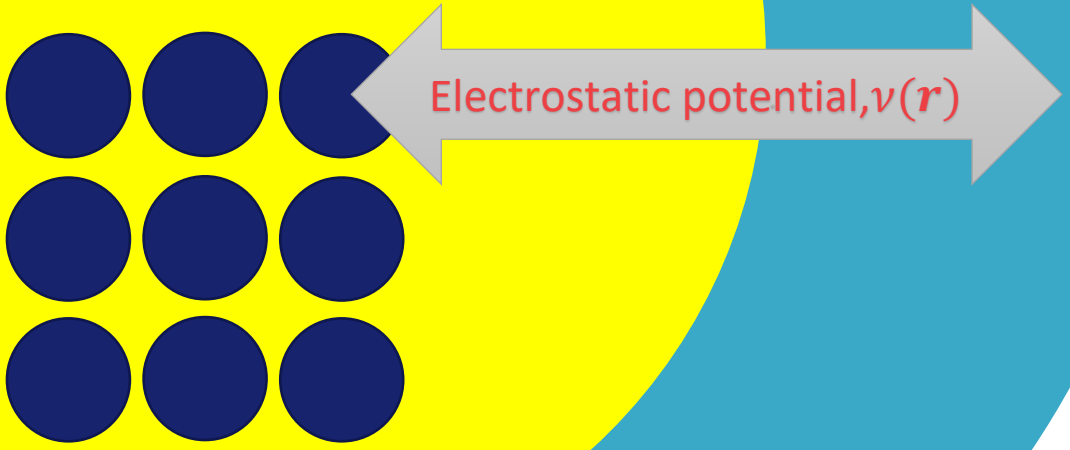

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$$+\sum_k f_k \int \psi_k^*(\boldsymbol{r})\, v_{\mathrm{ps}}(\boldsymbol{r})\, \psi_k(\boldsymbol{r}) d\boldsymbol{r}$$ Pseudopotential contribution

$$+E_{\mathrm{xc}}$$ Exchange Correlation Energy

$$+\int \left[-\frac{\varepsilon(\boldsymbol{r})|\nabla v(\boldsymbol{r})|^2}{8\pi} + \rho(\boldsymbol{r})v(\boldsymbol{r}) + \sum_{i=1}^{p} z_i c_i(\boldsymbol{r})\, v(\boldsymbol{r})\right] d\boldsymbol{r}$$ Electrostatic En.

$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) d\boldsymbol{r}$$ Electrolyte osmotic pressure

$$-k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln \lambda(\boldsymbol{r})\, d\boldsymbol{r}$$ Electrolyte accessibility term

$$+k_B T \sum_{i=1}^{p} \int c_i(\boldsymbol{r}) \ln\left(\frac{c_i(\boldsymbol{r})}{c^{\mathrm{o}}}\right) d\boldsymbol{r}$$ Electrolyte entropy

$$-\sum_{i=1}^{p} \mu_i \int c_i(\boldsymbol{r}) d\boldsymbol{r}$$ Electrolyte chemical potential

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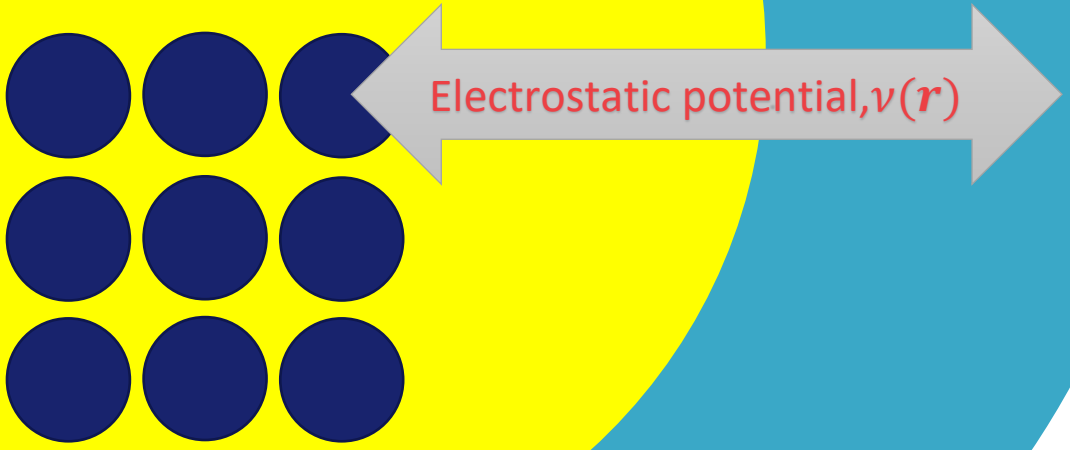

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$$+k_B T \sum_k f_k \ln f_k + (1 - f_k) \ln f_k$$ Entropy

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$$+\gamma S$$ Solvent cavitation, dispersion and repulsion

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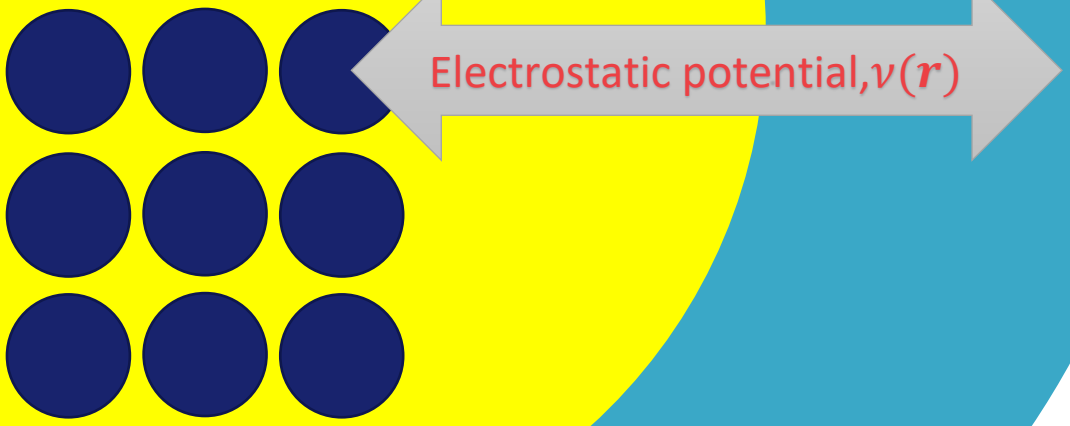


Electrostatic potential, $v(\boldsymbol{r})$

Dielectric solvent $\varepsilon(\boldsymbol{r})$
and
Continuum electrolyte

$z_i, c_i(\boldsymbol{r}), i = 1 \ldots p$

Total free energy,

$\Omega[\psi_{\mathrm{k}}(\boldsymbol{r}), f_k, v(\boldsymbol{r}), c_i(\boldsymbol{r})]$

is minimized

Grand canonical DFT

$$\left[-\frac{1}{2}\nabla^2 + v_{\mathrm{ps}}(\boldsymbol{r}) + v_{\mathrm{xc}}(\boldsymbol{r}) + v(\boldsymbol{r})\right]\psi_k = \varepsilon_k \psi_k$$

$$f_k = \frac{1}{1 + \exp\left(\frac{\varepsilon_k - \mu_{\mathrm{e}}}{k_{\mathrm{B}}T}\right)}$$

$$\mu_{\mathrm{e}} = \mu_{\mathrm{e}}^{\mathrm{ref}} - e \cdot U$$

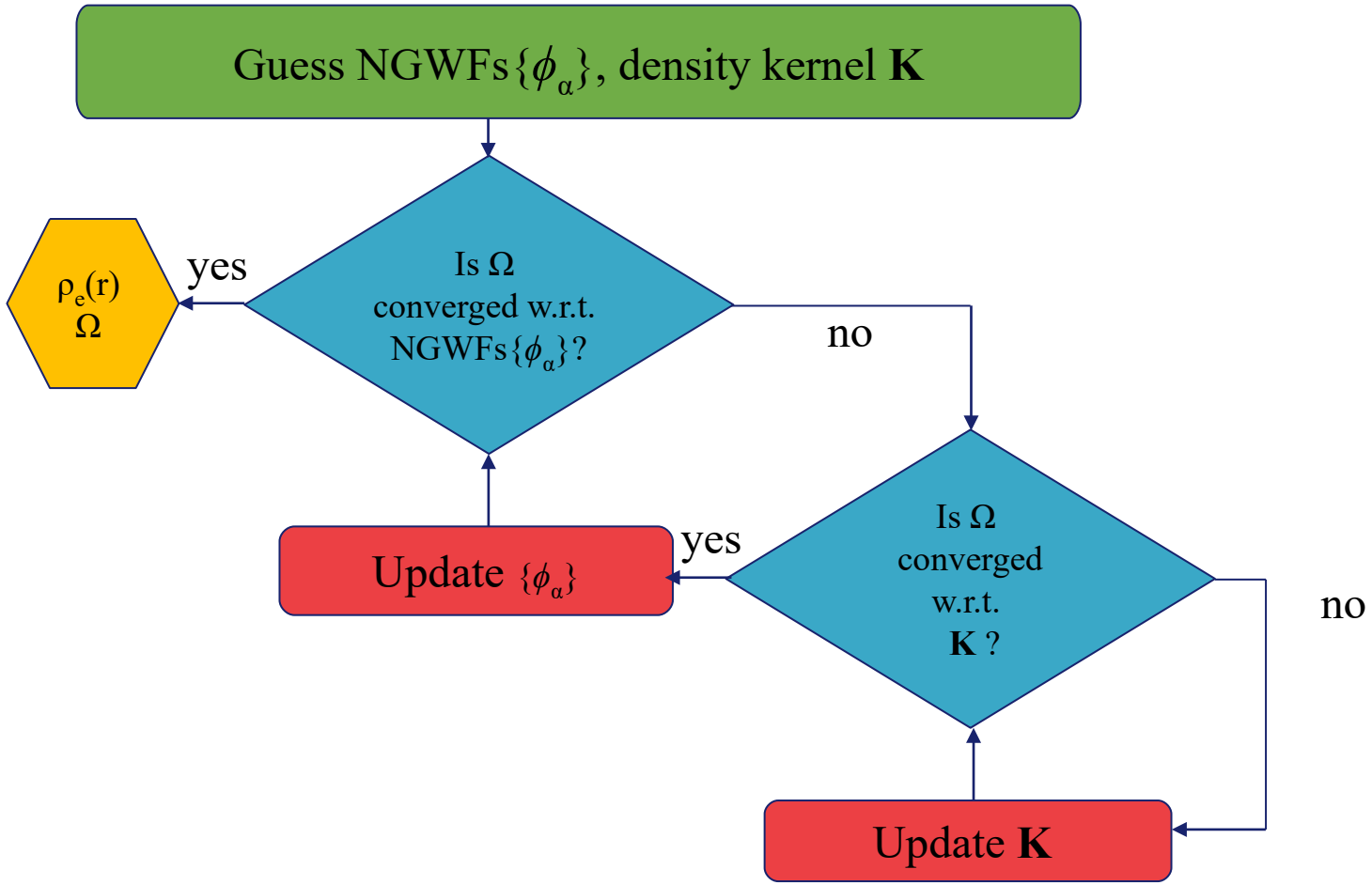
Poisson-Boltzmann Theory

$$\nabla.[\varepsilon(\boldsymbol{r})\nabla v(\boldsymbol{r})] = -4\pi\left[\rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r}) + \sum_{i=1}^{p} z_i c_i(\boldsymbol{r})\right]$$

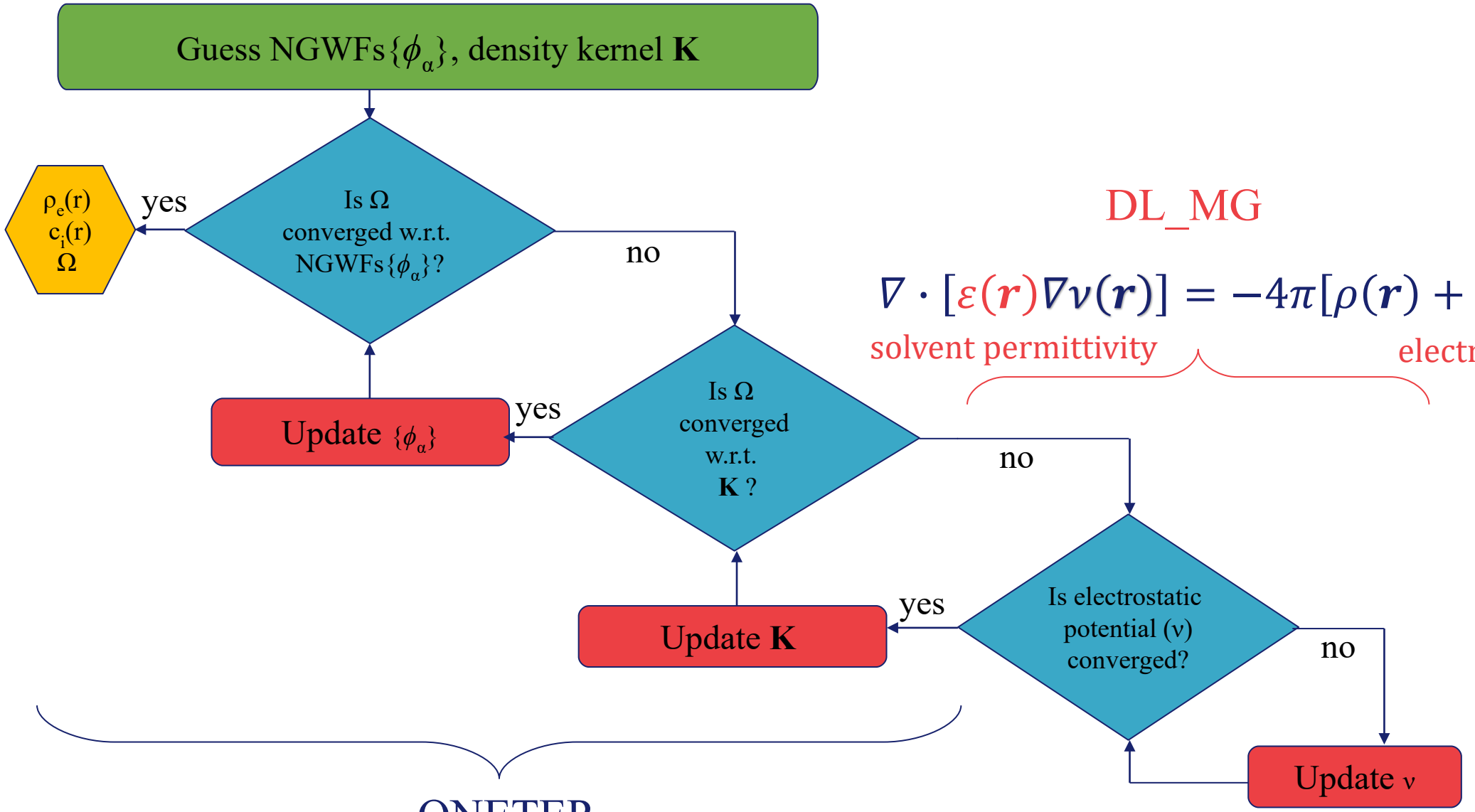
$$c_i(\boldsymbol{r}) = \lambda(\boldsymbol{r}) c_i^{\infty} \exp\left(\frac{-z_i[v(\boldsymbol{r}) + v_{\mathrm{s}}]}{k_B T}\right)$$

$$\int_V \left[\rho_{\mathrm{e}}(\boldsymbol{r}) + \rho_{\mathrm{nuc}}(\boldsymbol{r}) + \sum_{i=1}^{p} z_i c_i(\boldsymbol{r})\right] d\boldsymbol{r} = 0$$

ONETEP Calculation procedure in vacuum



ONETEP Calculation procedure with new electrolyte model

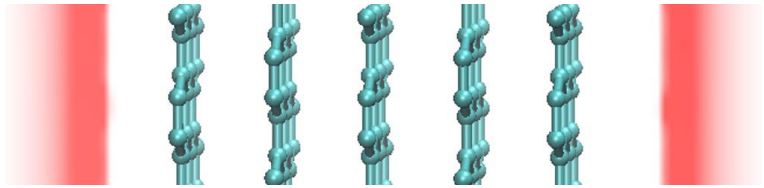


DL_MG

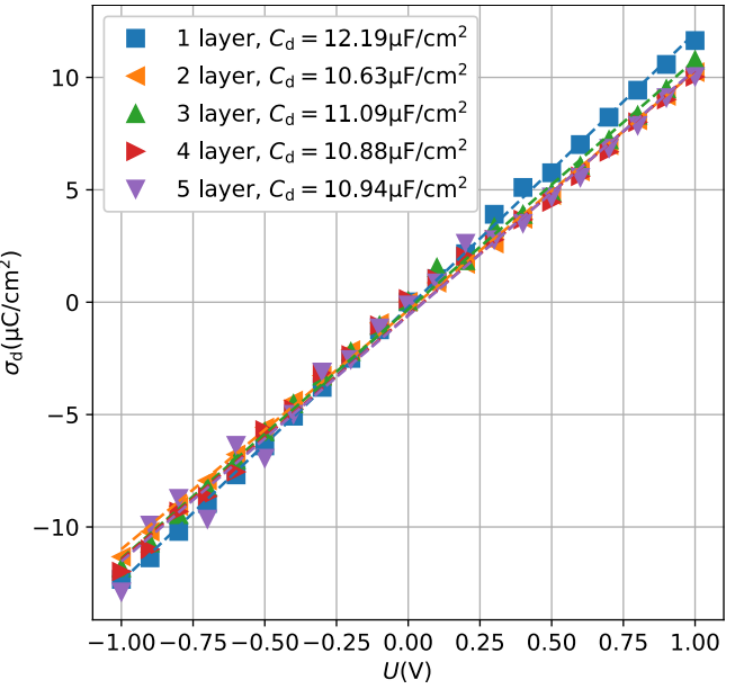
$$\nabla \cdot [\varepsilon(\boldsymbol{r})\nabla\nu(\boldsymbol{r})] = -4\pi[\rho(\boldsymbol{r}) + \rho_{mob}(\boldsymbol{r})]$$

solvent permittivity — electrolyte charge

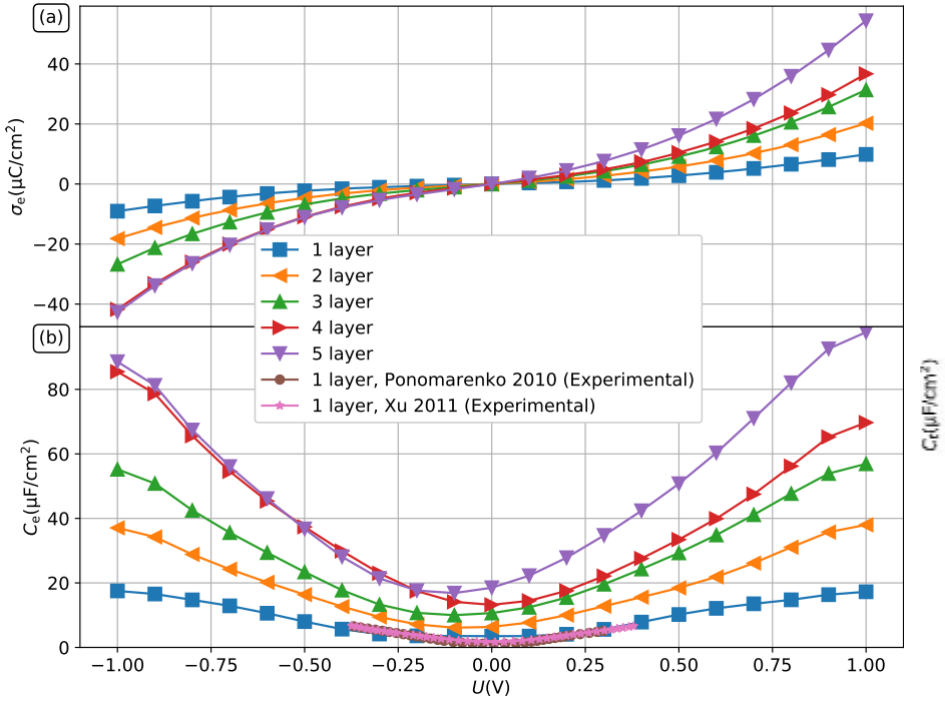
Differential capacitance of few-layer graphene



Diffuse layer capacitance (C_d)



Electronic capacitance (C_e)



The Journal of Chemical Physics ARTICLE scitation.org/journal/jcp

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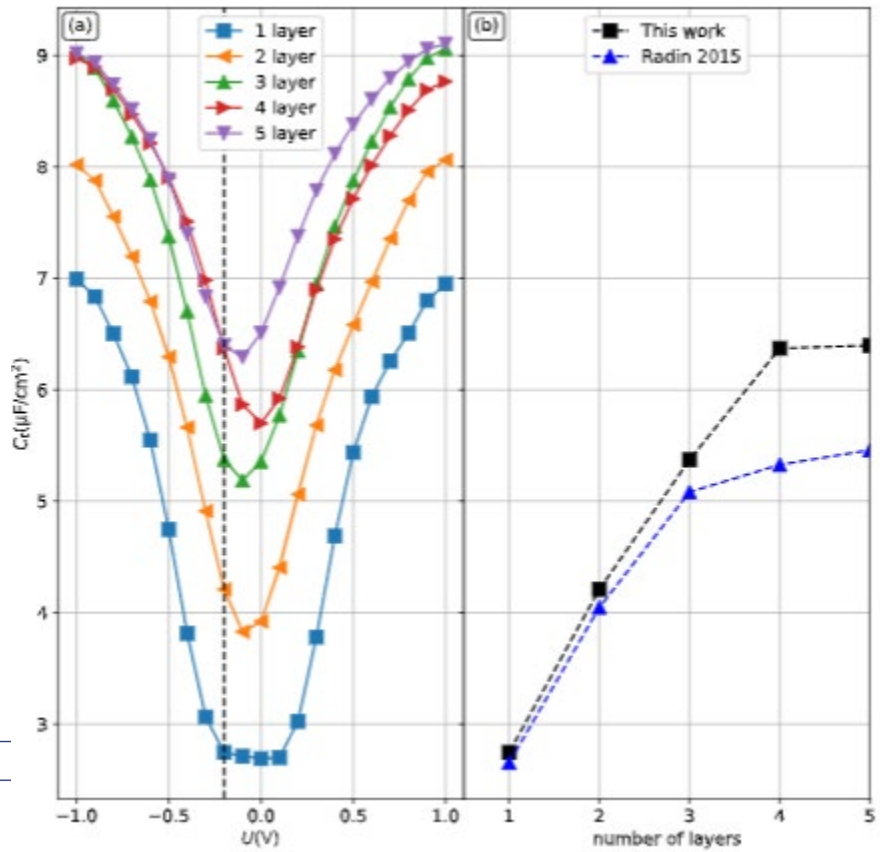
Arihant Bhandari,[1,2] Chao Peng,[3,2] Jacek Dziedzic,[1,4,2] Lucian Anton,[5] John R. Owen,[1,2] Denis Kramer,[3,2,6] and Chris-Kriton Skylaris[1,2,a)]

Total capacitance $\frac{1}{C_t} = \frac{1}{C_d} + \frac{1}{C_e}$



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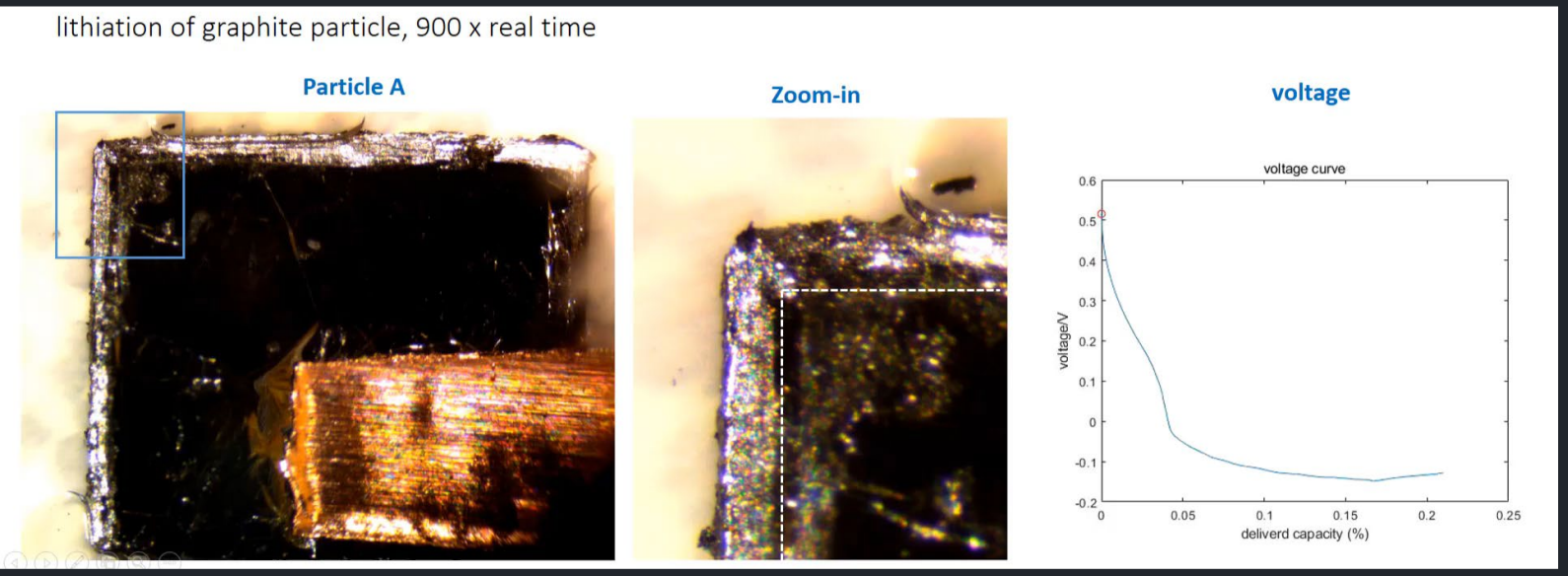
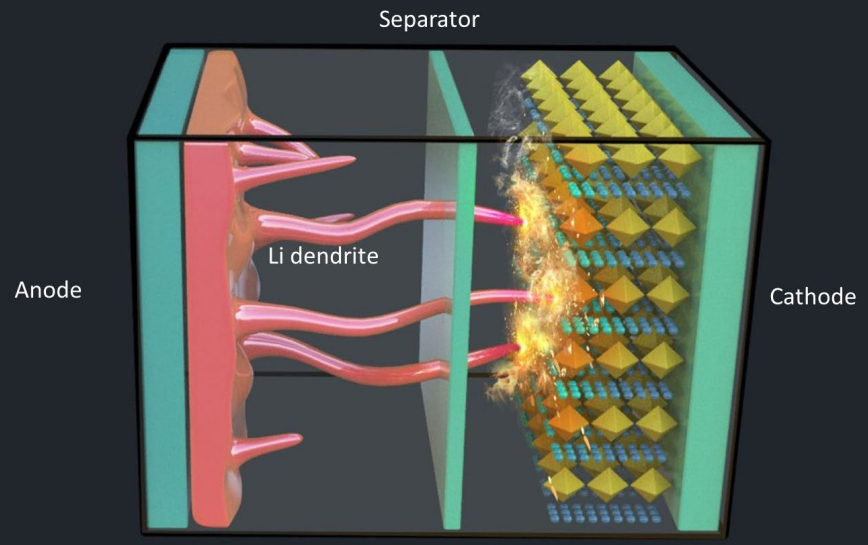
Li plating and dendrite growth on graphite





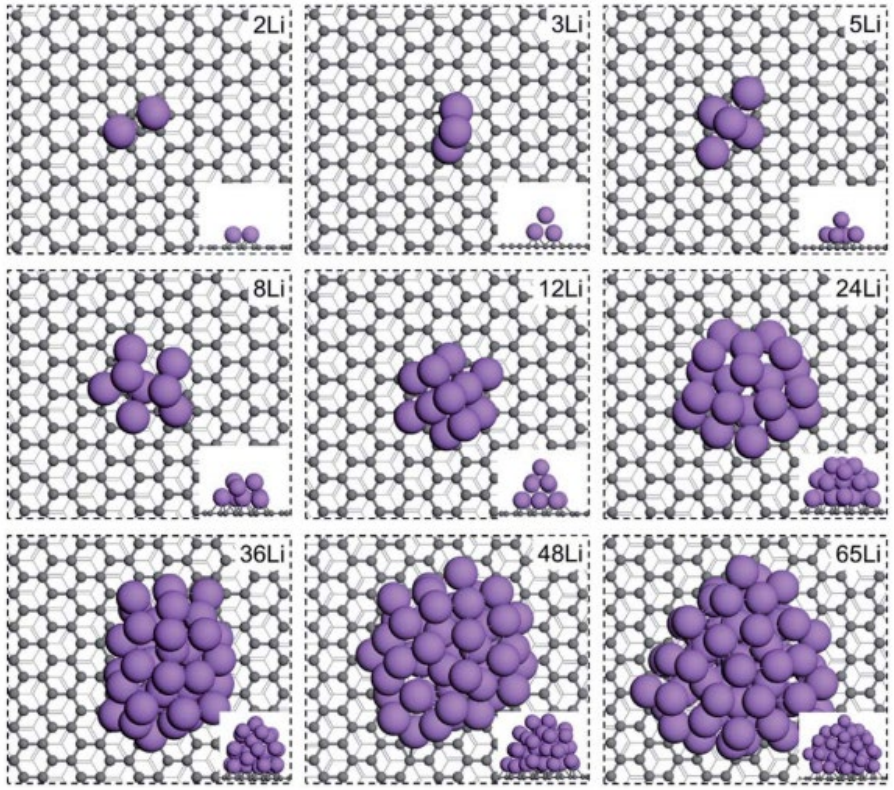
Gao et al. Joule 5, 393–414, (2021)

WHAT ARE THE CONDITIONS FOR DENDRITE GROWTH IN LI-ION BATTERIES

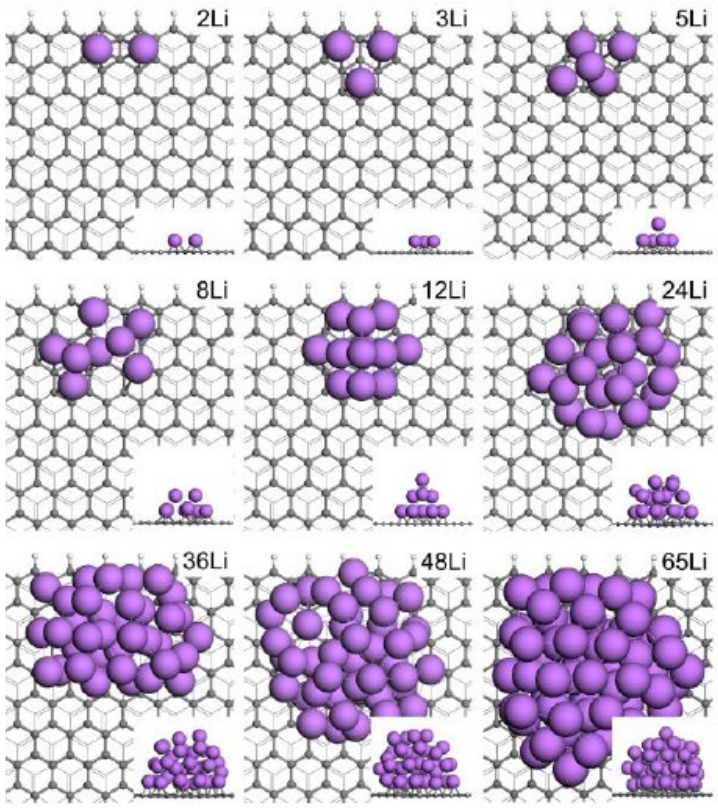
- At what voltage with respect to Li/Li^+ does the nucleation of Li clusters start?
- What is the voltage for onset of dendrite growth in a battery?
- At what location on a graphite particle do dendrites grow?
- What is the effect of electrolyte?
- How can it be prevented?

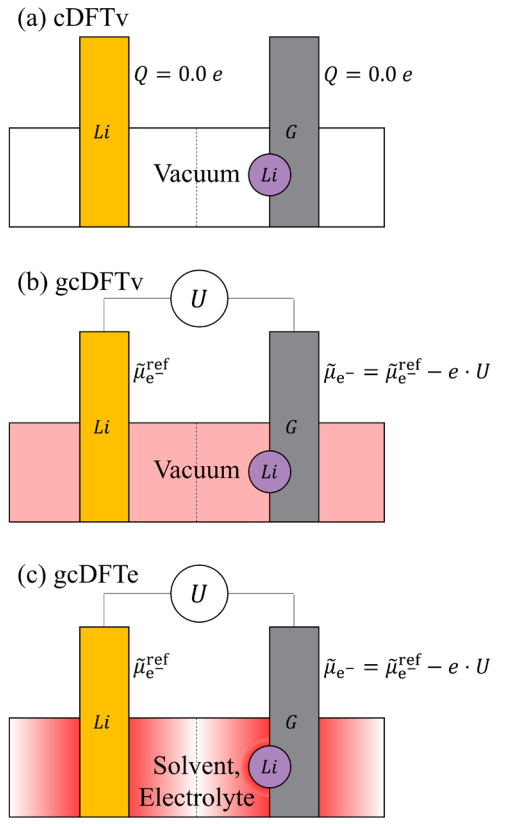
What are the conditions for dendrite growth in Li-ion batteries

- On extended basal plane



- Close to zigzag edge





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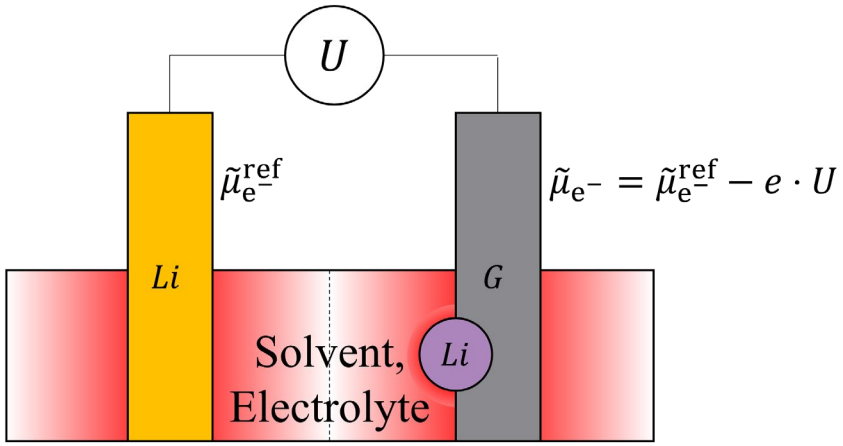
Li nucleation on the graphite anode under potential control in Li-ion batteries†

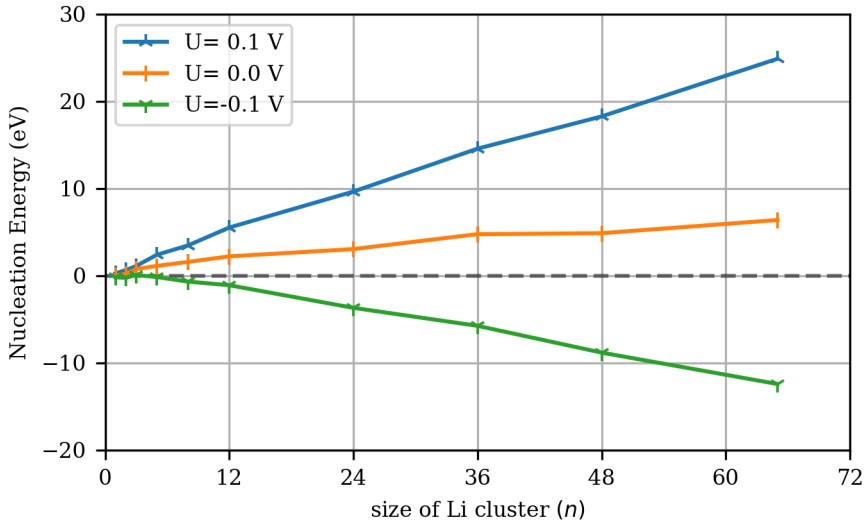
Arihant Bhandari, [ab] Chao Peng, [bc] Jacek Dziedzic, [abd] John R. Owen, [ab] Denis Kramer [bce] and Chris-Kriton Skylaris [*ab]



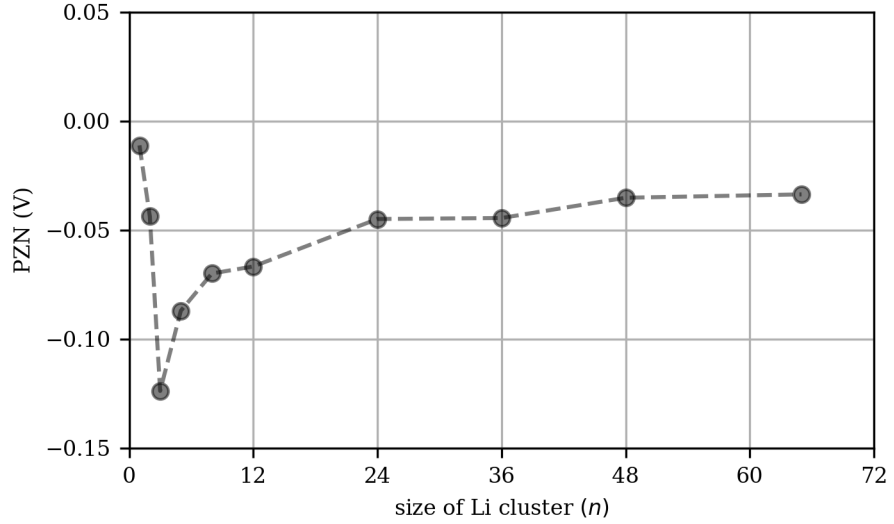
$$n\,Li + G \rightarrow Li_nG,$$

$$\Delta\Omega(U) = \left[\Omega_{Li_nG}(U) - \Omega_G(U) - n \cdot \left(\tilde{\mu}_{Li}^{ref}\right)\right]$$

Nucleation energy (ΔΩ)

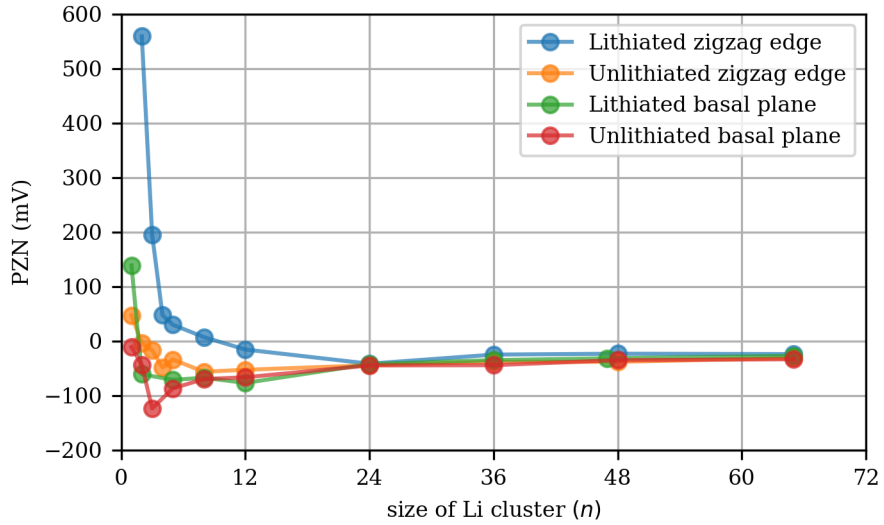


Potential of zero nucleation energy (PZN)



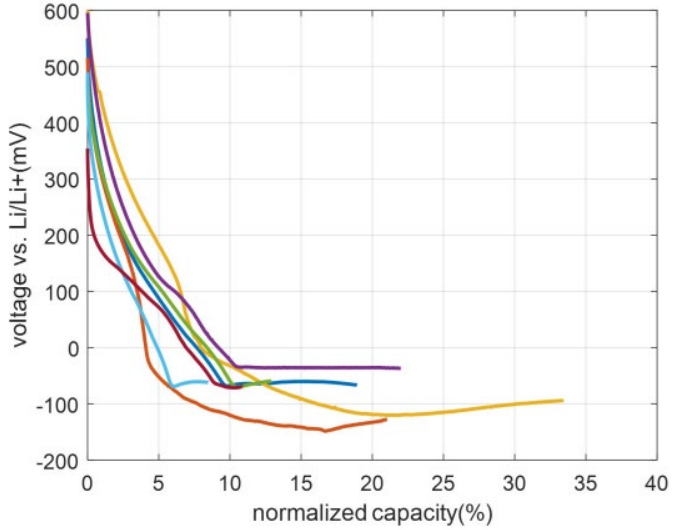
POTENTIAL OF ZERO NUCLEATION ENERGY (PZN)

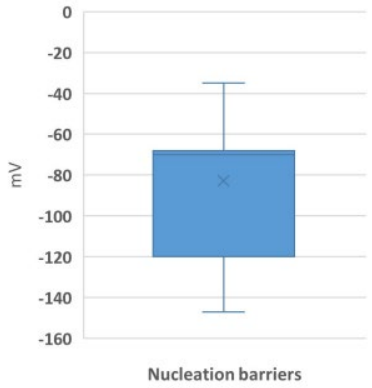
Computed, Bhandari et al. JMCA 10, 11426, 2022



Zigzag edge	Lithiated graphite	-40 mV
	Unlithiated graphite	-60 mV
Basal plane	Lithiated graphite	-80 mV
	Unlithiated graphite	-120 mV

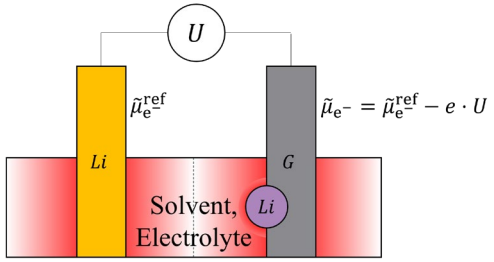
Experimental, Gao et al. Joule 5, 393, 2021



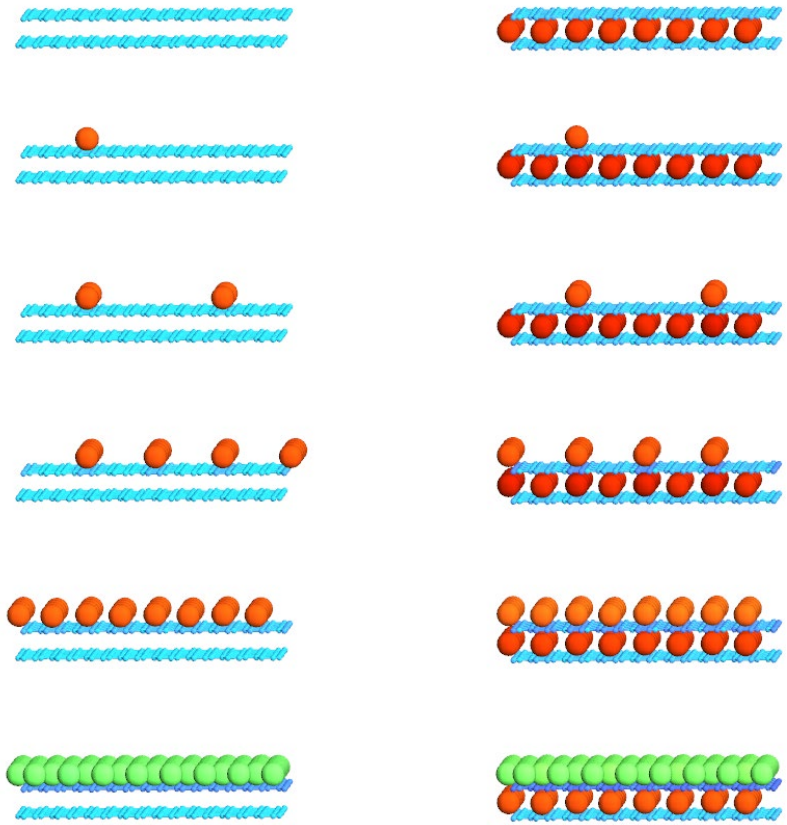


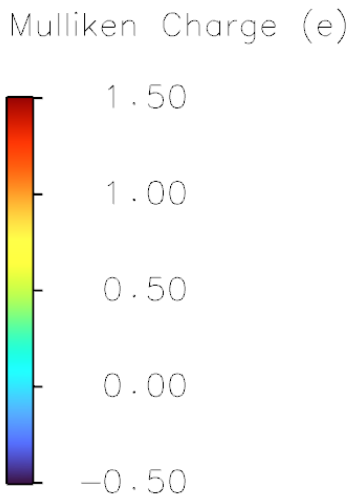
Mechanisms of Li deposition on graphite

Surface coverage



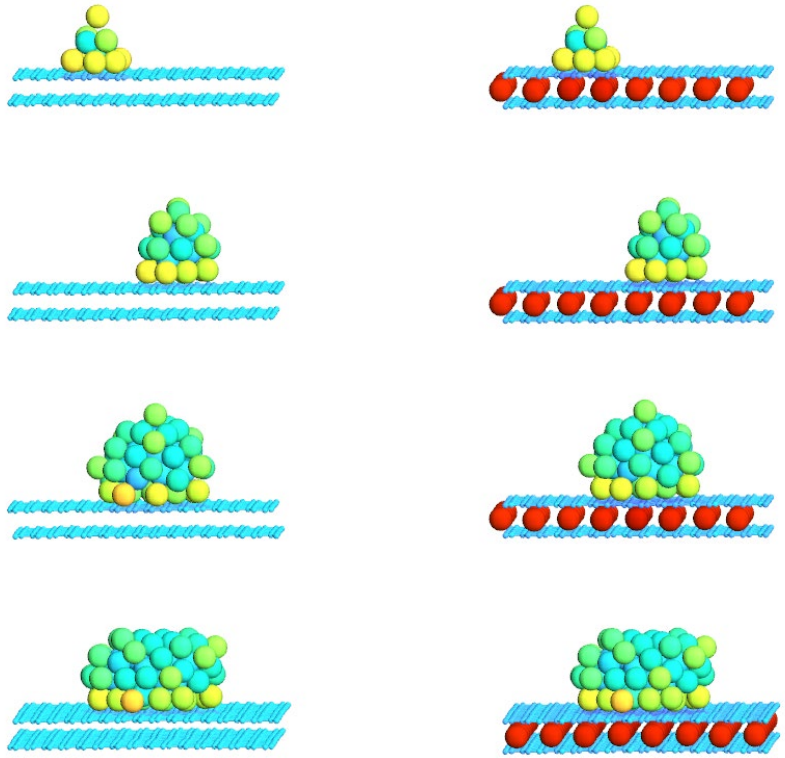
(a) Unlithiated graphite (b) Lithiated graphite





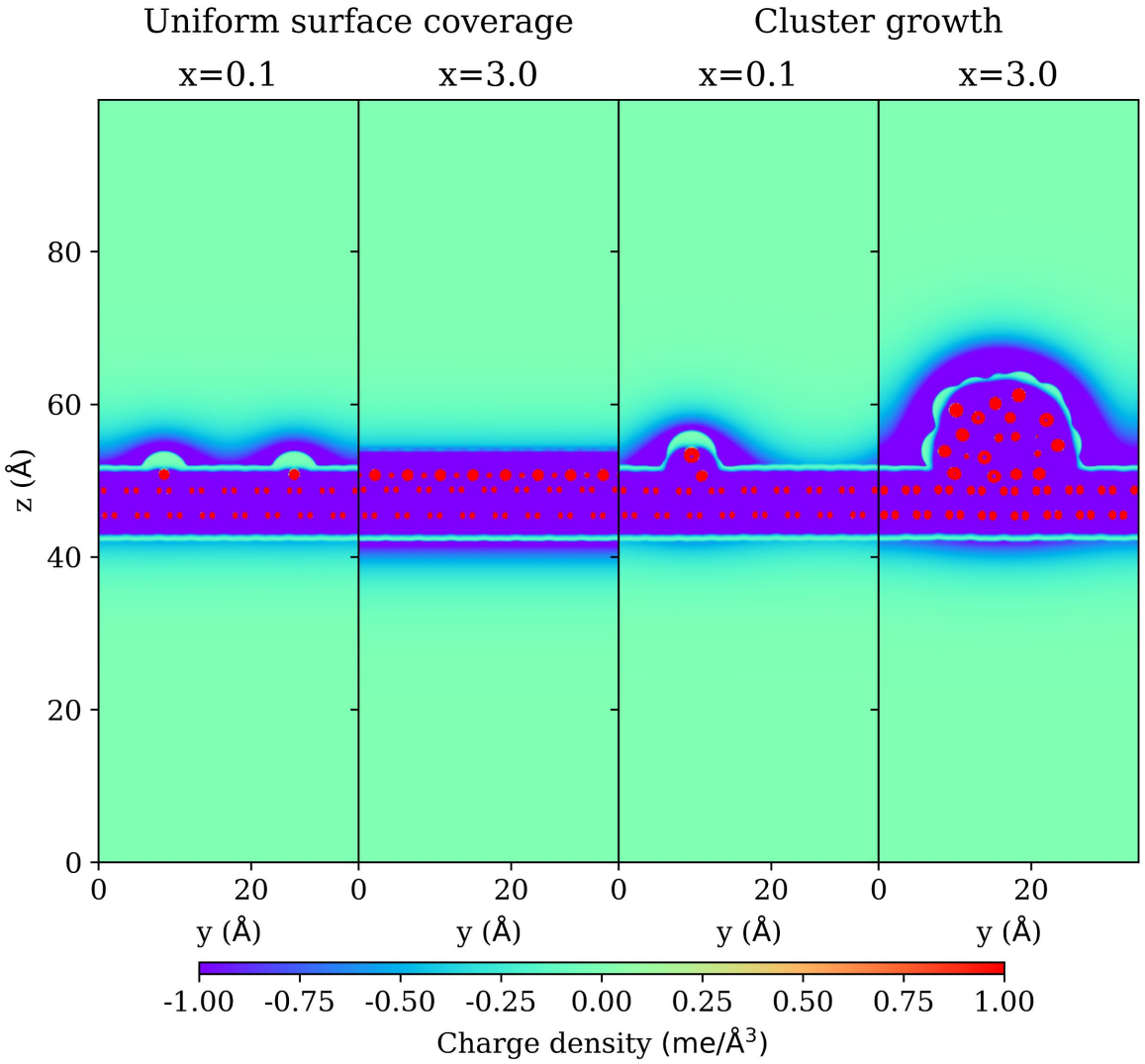
Cluster growth

(a) Unlithiated graphite (b) Lithiated graphite

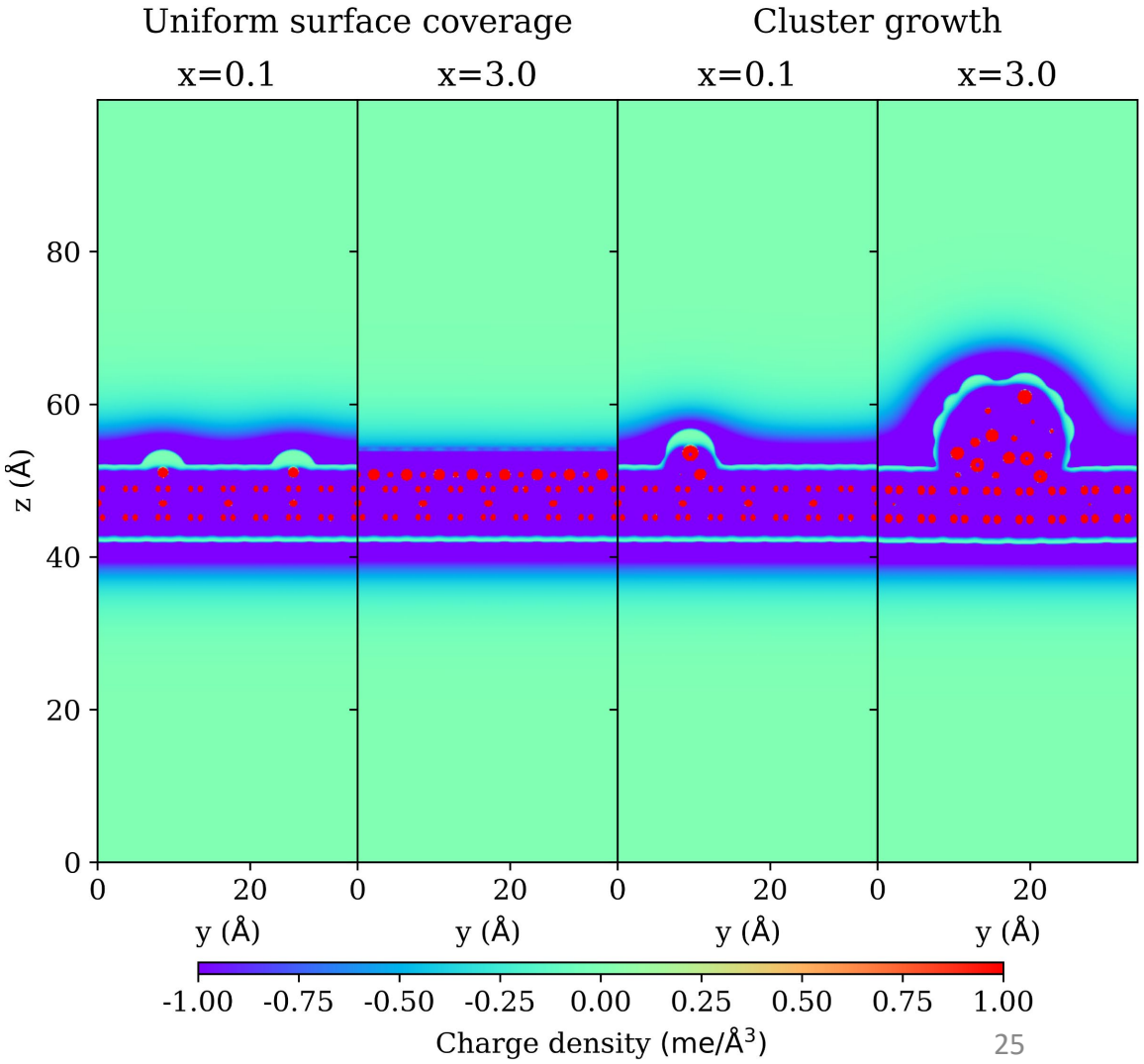


Total charge density

Unlithiated graphite



Lithiated graphite



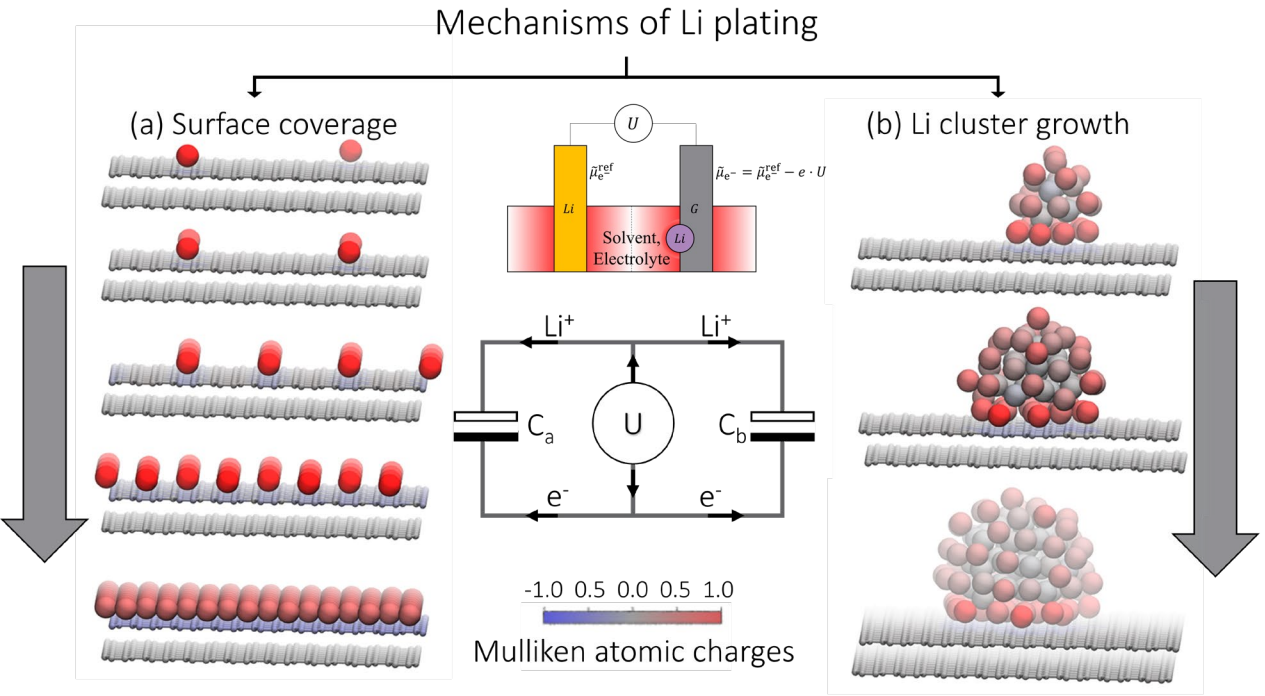
Mechanisms of Li deposition: surface coverage and dendrite growth

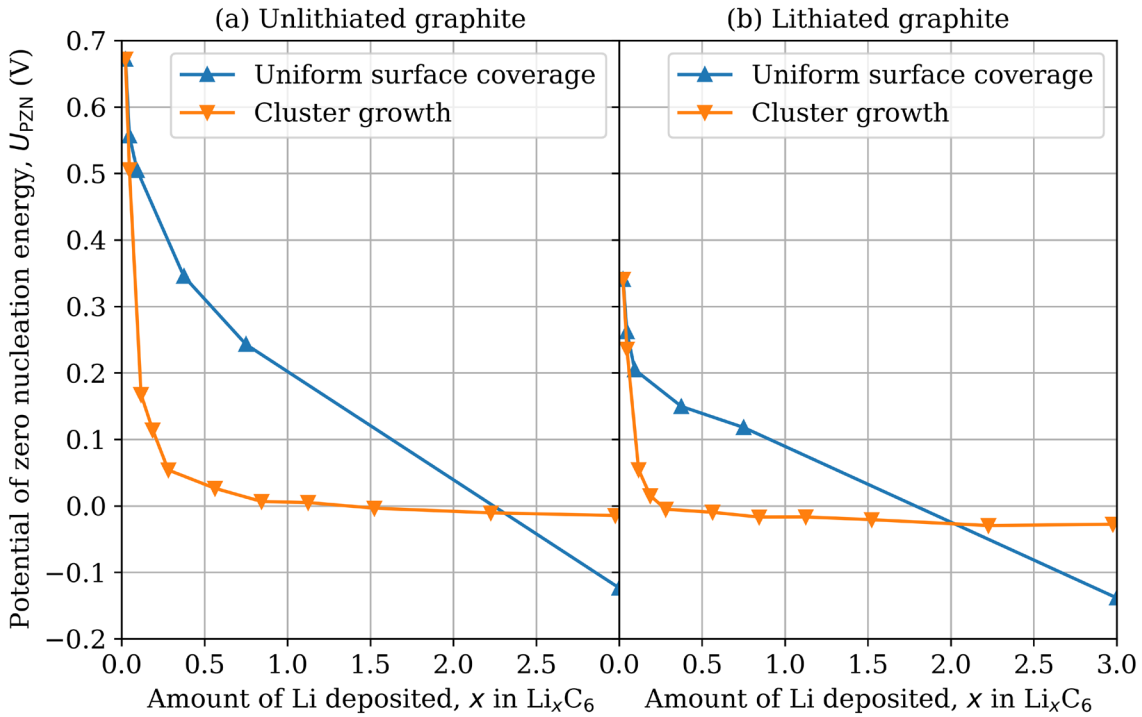
Arihant Bhandari, Jacek Dziedzic, John R. Owen, Denis Kramer, Chris K. Skylaris, *J. Mater. Chem. A (Under review)*

We find that the process of Li deposition on graphite anode occurs in following stages:

- Deposition of Li-ions uniformly on the surface of graphite anode at higher voltages (> 0.0 V)
- Reduction of aggregated Li-ions to metallic Li clusters and growth of Li clusters into dendrites (< 0.0 V)

We find the cross-over voltage for the above two processes. For safe operation of Li-ion batteries the voltage on graphite should be kept above this cross over value.





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