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# CONP2: Fast Simulations Of Constant Potential Difference Conductive Electrodes

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# Outline

1. Build a capacitor
2. Charge it up
3. Get awesome results
4. Make it faster
5. Some interesting systems
6. What's in the works?

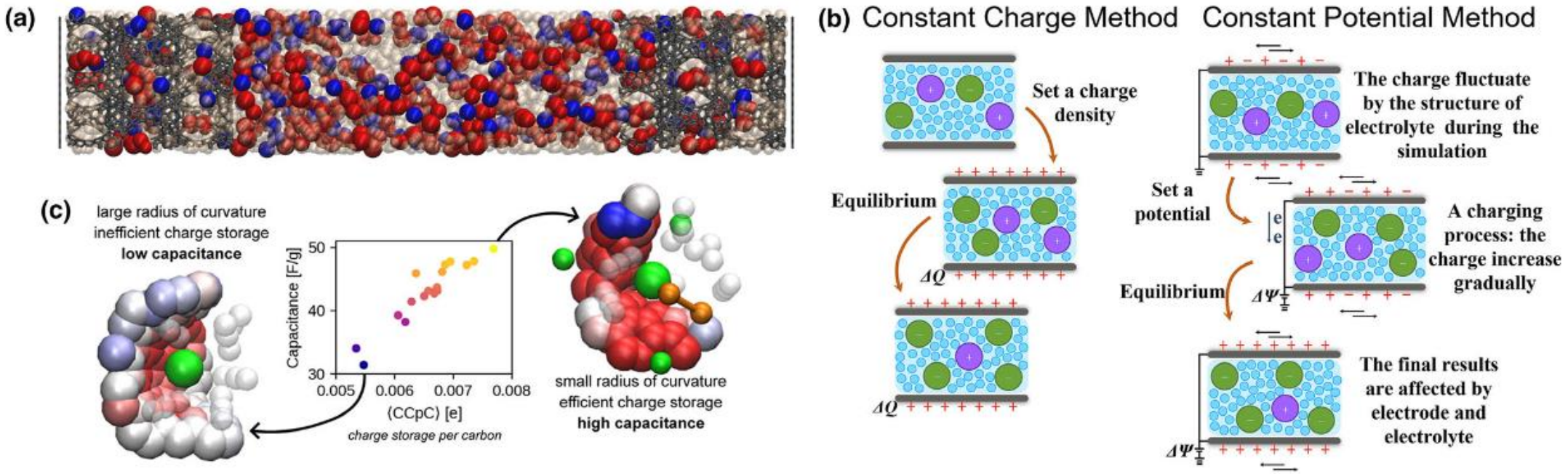



**Figure 1.** a) A common simulation setup for EDL capacitors, the electrode on each side can be graphene, porous carbon, or MXene material, etc., the electrolytes can be aqueous, organic or neat ionic liquid. Reproduced with permission.[56] Copyright 2019, American Chemical Society. b) Schematic diagram of the simulation process and electrode charge evolution with CCM and CPM. Reproduced with permission.[47] Copyright 2017, Wiley. c) Snapshots of charge compensation per carbon (CCpC) of carbon pore with large and small radii. The carbon atom of the pore is colored according to their induced charge, with red indicating positive and blue indicating negative, scaled from −0.01 to 0.01 e.

Xu et al. (2020), Energy Environ. Mater., 3: 235-246.

# Notes about history

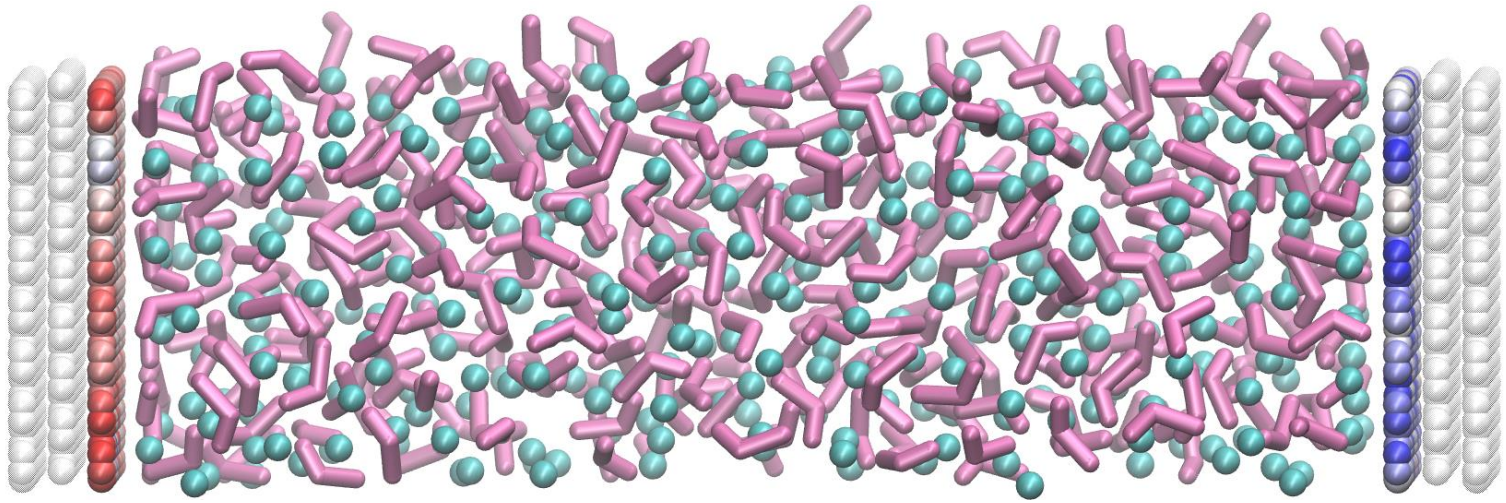
Original plugin was LAMMPS-CONP
(https://github.com/zhenxingwang/lammps-conp)

New version introduces:

- Electroneutrality constraint
- Support for hybrid pair styles, “newton on” and Intel acceleration
- Dedicated kspace pppm style for direct interfacing
- Support for specialised periodic boundary conditions
- Support for equal-style potential differences (ramp / oscillating potentials)
- compute potential/atom to measure electric potential experienced by an atom

# Building a capacitor

**Electrolyte**: water, water-in-salt, ionic liquid, diluted ionic liquid …



**Electrode**: graphite layers, metal interfaces, porous electrodes …

Create separate groups for left and right electrodes.

“eleleft”

“eleright”

# Charge it up!

```
# Get solvent and electrode groups
group sol molecule 1:200
group eleleft molecule 201
group eleright molecule 202

# Call constant potential fix
fix conp eleleft conp 1 eleright 1.979 1.0 log_conp

# Compute right electrode charge
# Electroneutrality guarantees qleft = -qright
compute qright reduce eleright q

# Print out charge in thermo
thermo_style custom step … c_qright

# Run NVT integration
fix nvt sol nvt ${temp} ${temp} ${tdamp}
```

**Syntax:**

fix [ID] [group1] conp [nsteps] [group2] [eta] [DV] [logfile]

**Notes:**

Fix conp automatically imposes a potential difference so that group2 is DV volts above group1

“eta” is an inverse length, typically set to 1.979 $Å^{-1}$ (but watch this space)

DV can be an equal style variable (ramps permitted!)

# Charge it up! (How it works)

Elec. potential is applied to electrode and the solution responds:

$$\mathcal{H} = K + U_0(\mathbf{r}_{sol}, \mathbf{r}_{el}) - \mathbf{q}_{el}^T \mathbf{\Psi} + U_{el}(\mathbf{q}_{sol}, \mathbf{r}_{sol}, \mathbf{q}_{el}, \mathbf{r}_{el})$$

$$U_{el} = \frac{1}{2}\mathbf{q}^T \mathbf{A} \mathbf{q} - \mathbf{q}^T \mathbf{B}(\mathbf{r})$$

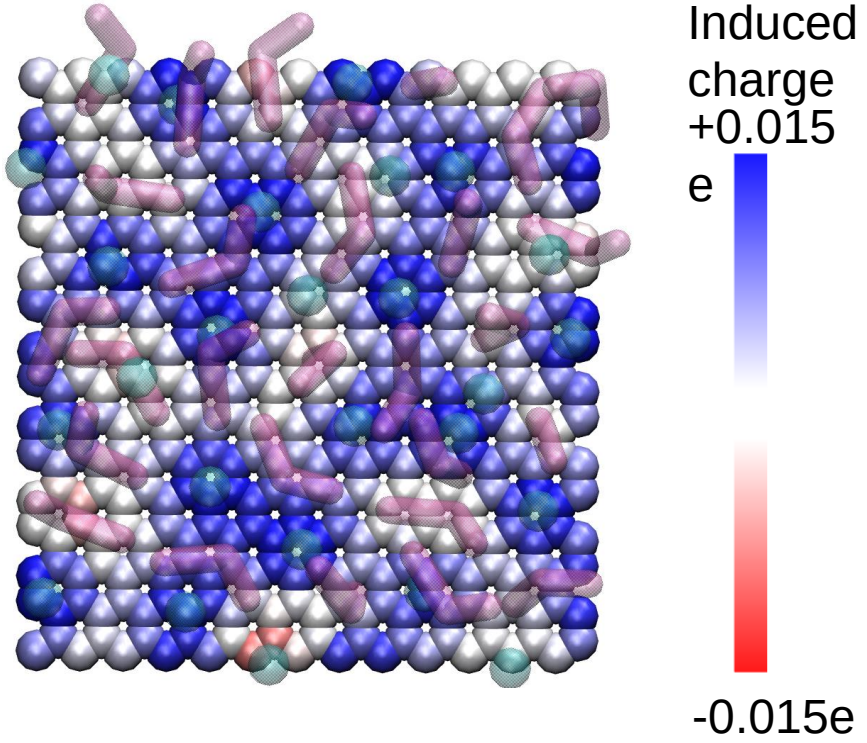
Conductive electrode (Born-Oppenheimer): at each timestep, $\partial U / \partial \mathbf{q} = 0$ and $\sum q = 0$

Constant potential: $\mathbf{\Psi} = \Delta\Psi \mathbf{D}$ where $\mathbf{D} = \frac{1}{2}(1, \ldots, 1, -1, \ldots, -1)$ is an "electrode indicator".

Solution:

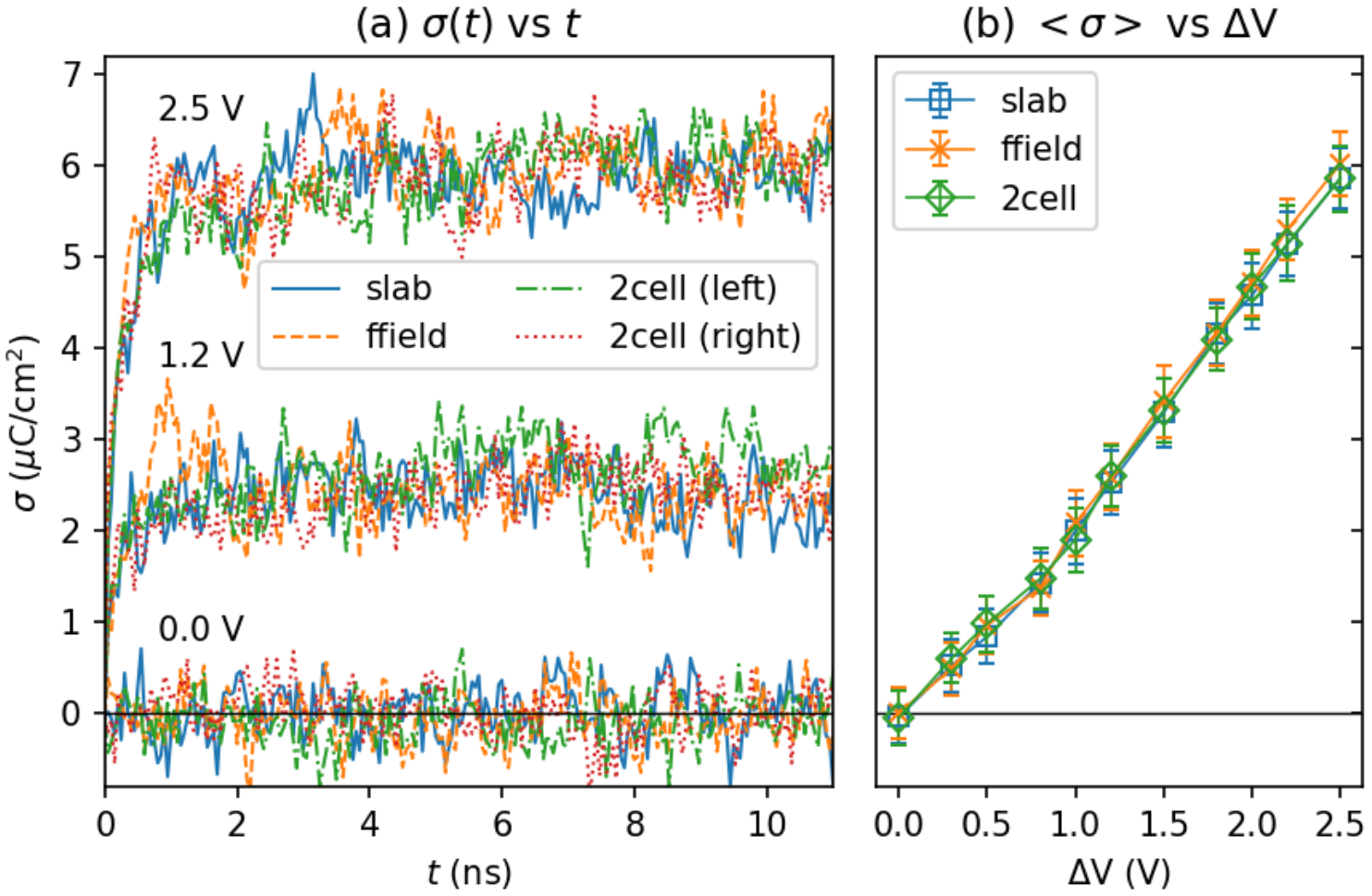
$$\mathbf{q}^* = \mathbf{A}_{\perp}^{-1}(\mathbf{B}(\mathbf{r}) + \Delta\Psi \mathbf{D})$$

where $\mathbf{A}_{\perp}^{-1}$ projects $\mathbf{q}^*$ into the $\sum q = 0$ space.




Siepman & Sprik: JCP **102**, 511 (1995)
Rotenberg et al.:
PRL **111**,106102 (2013);
J Phys Chem C **118** (32), 18291–18298 (2013);
PCCP Advance Article (2020)

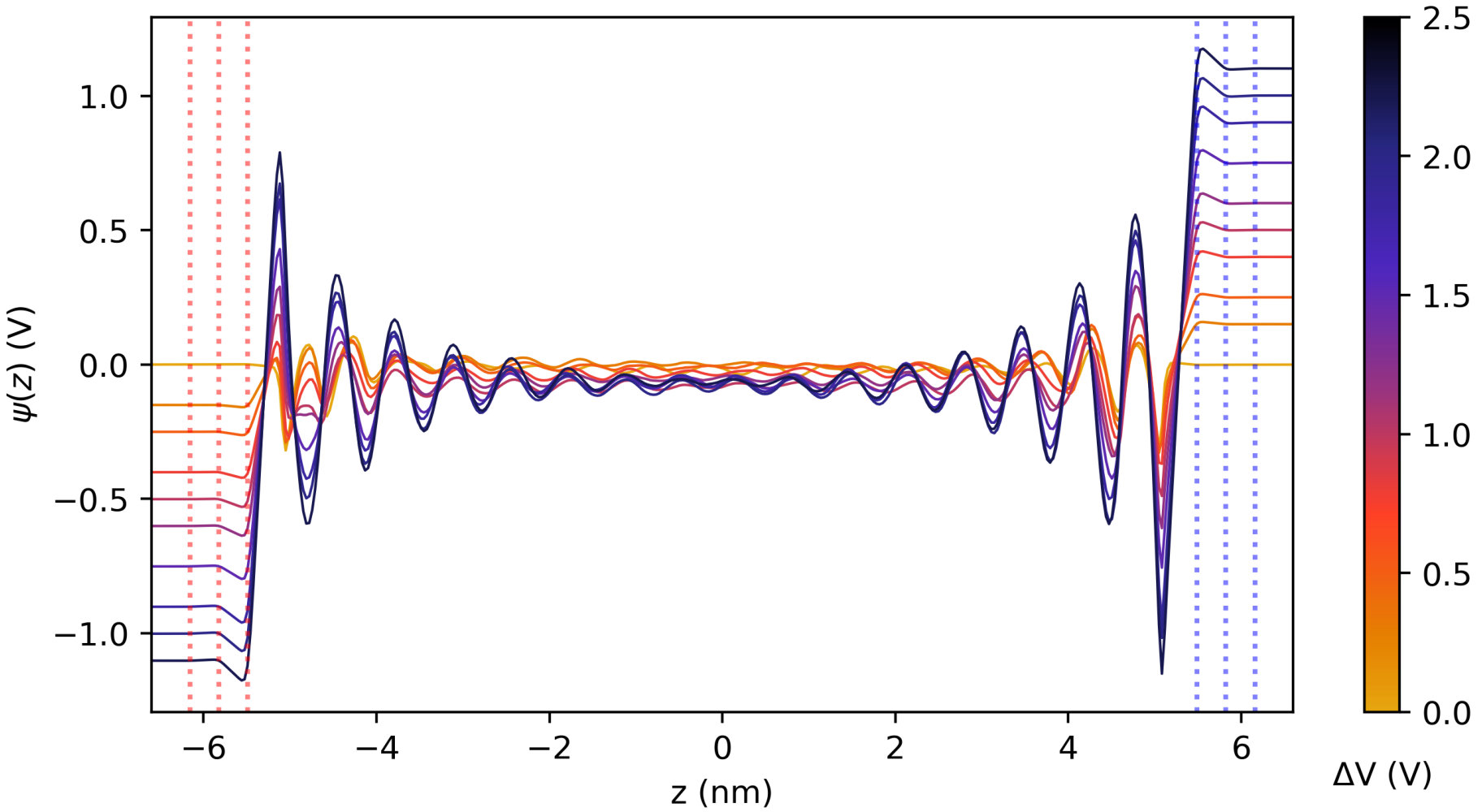
# Get awesome results!




A nanocapacitor in-silico!
With physically realistic:

- Charging / discharging time
- Johnson-Nyquist noise
- Voltage-dependent capacitance

# Get awesome results!

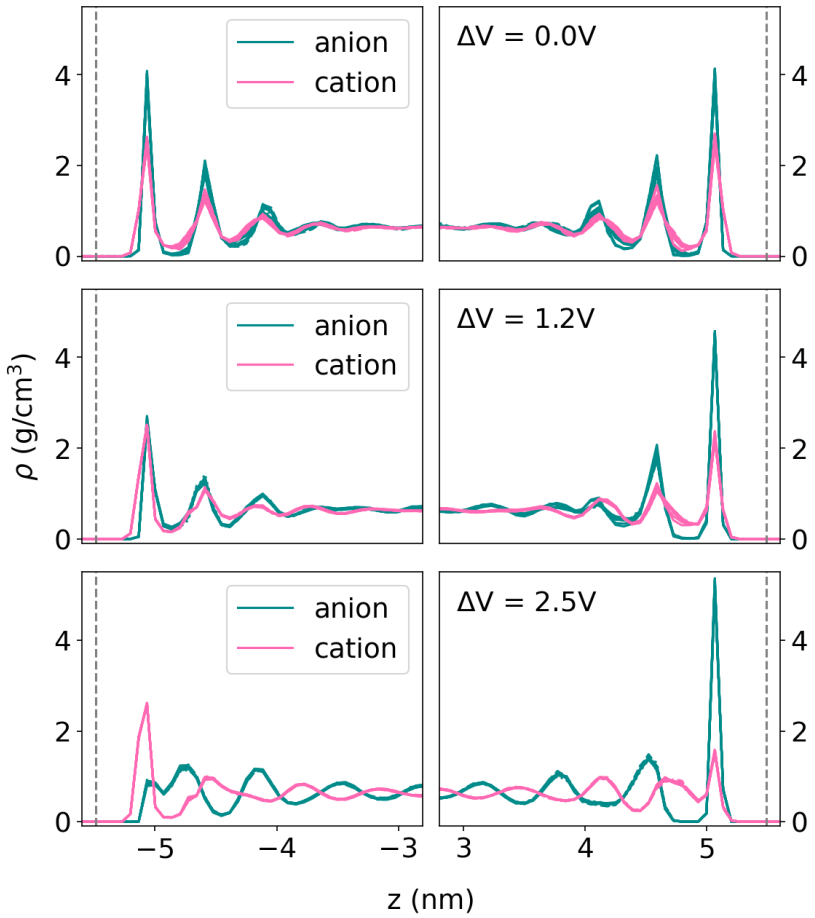


# Get awesome results!

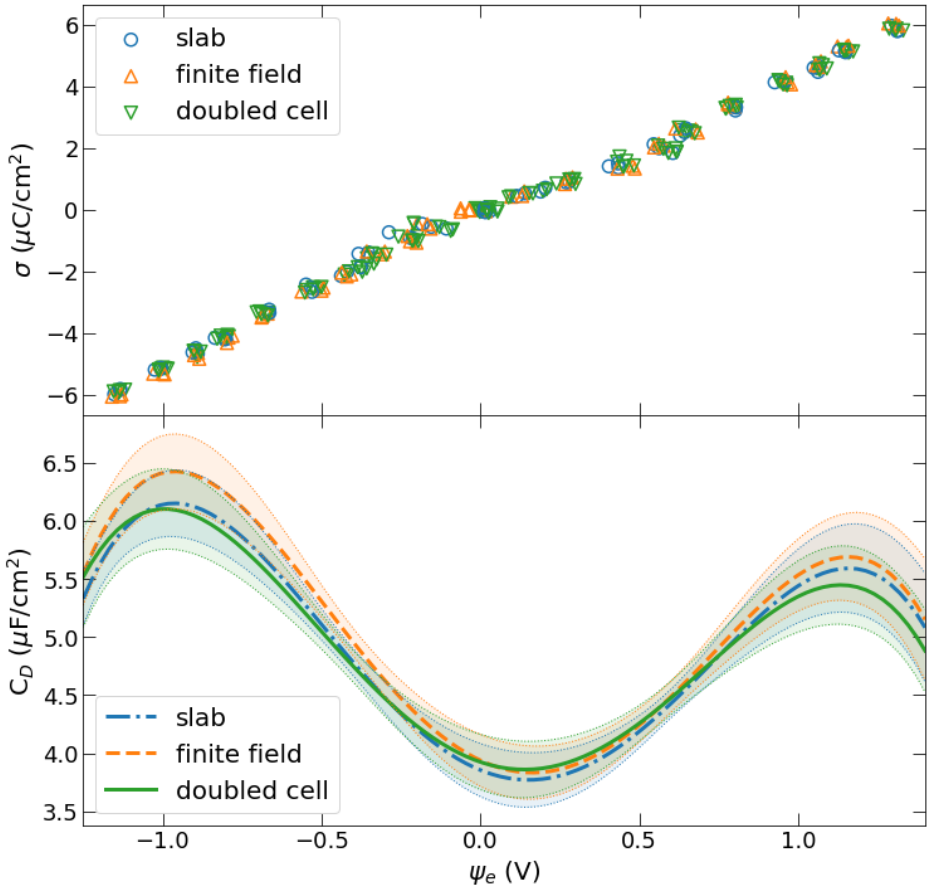
```
# set up lattice of probes
variable spacing_x equal lx/${nprobe_x}
variable rspacing_y equal (ly/${nprobe_y})/${spacing_x}
variable rspacing_z equal (lz/${nprobe_z})/${spacing_x}
Lattice custom ${spacing_x} a1 1 0 0 &
  a2 0 ${rspacing_y} 0 a3 0 0 ${rspacing_z} basis 0.5 0.5 0.5
variable n_atoms equal count(all)
Variable old_n_atoms equal $(v_n_atoms)
create_atoms 1 box
group probes id $(v_old_n_atoms+1):$(v_n_atoms)
neigh_modify exclude group probes probes
compute cz all chunk/atom bin/1d z center 0.005 units reduced


# set up potential compute and z-profile fix
compute potprobes probes potential/atom eta 1.979 eleleft eleright
fix potprofile probes ave/chunk ${nsteps} ${nsamples} &
    ${nstepsample} cz c_potprobes ave one

# works with rerun - even if only electrolyte positions recorded!
```

# Get awesome results!

## Electric layer structures




## Per-electrode Differential Capacitance



# Have I got alternatives?

## Fixed charge electrodes?

Pros:

- Slightly easier to use and understand
- Faster (but see later)

Cons:

- No obvious real-time equilibration
- Have to post-process for voltage
- Not applicable to complicated morphologies and charging / fluid dynamics

## What about other software?

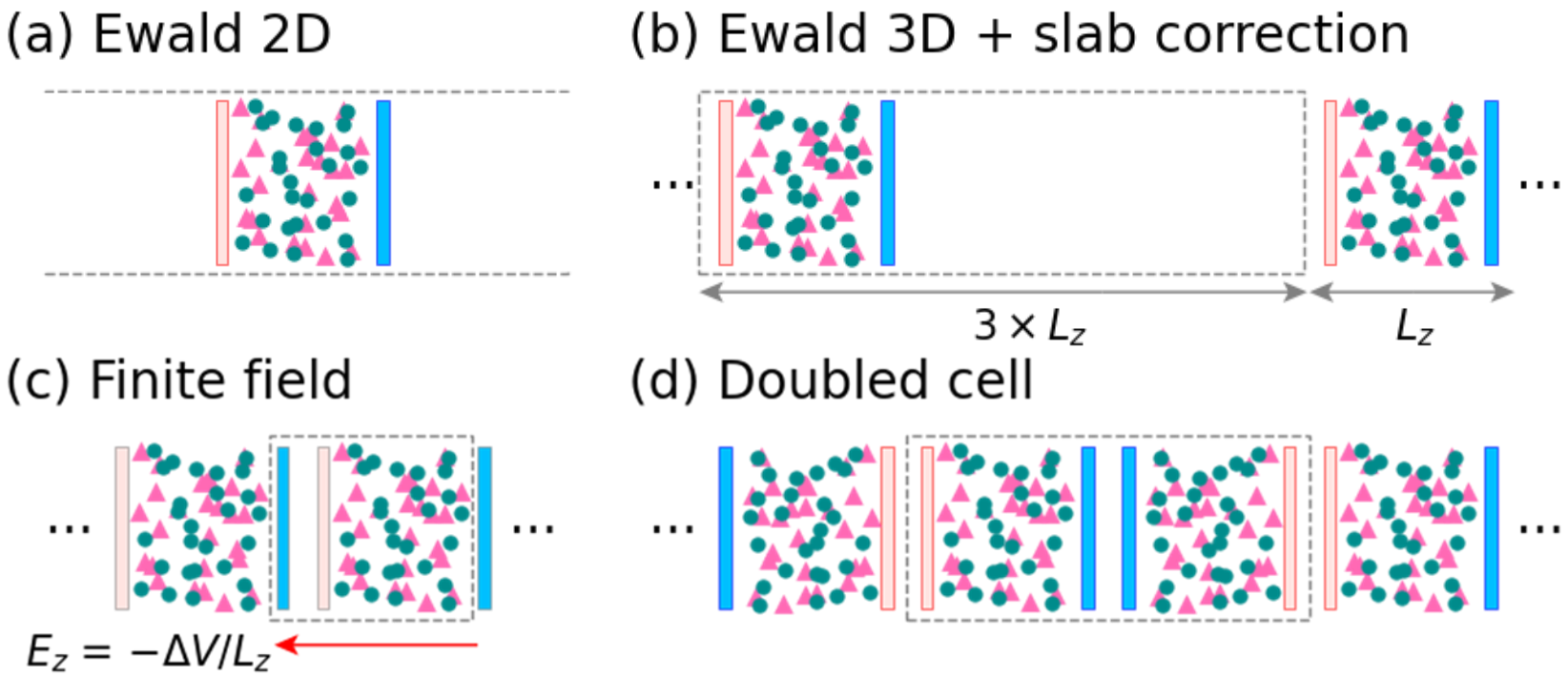
In LAMMPS:

- DIELECTRIC
- Image charges & electrode boundaries (Github kdwelle/lammps-fixes)
  - Only for planar electrodes

Outside LAMMPS: MetalWalls!

# Add secret sauce:

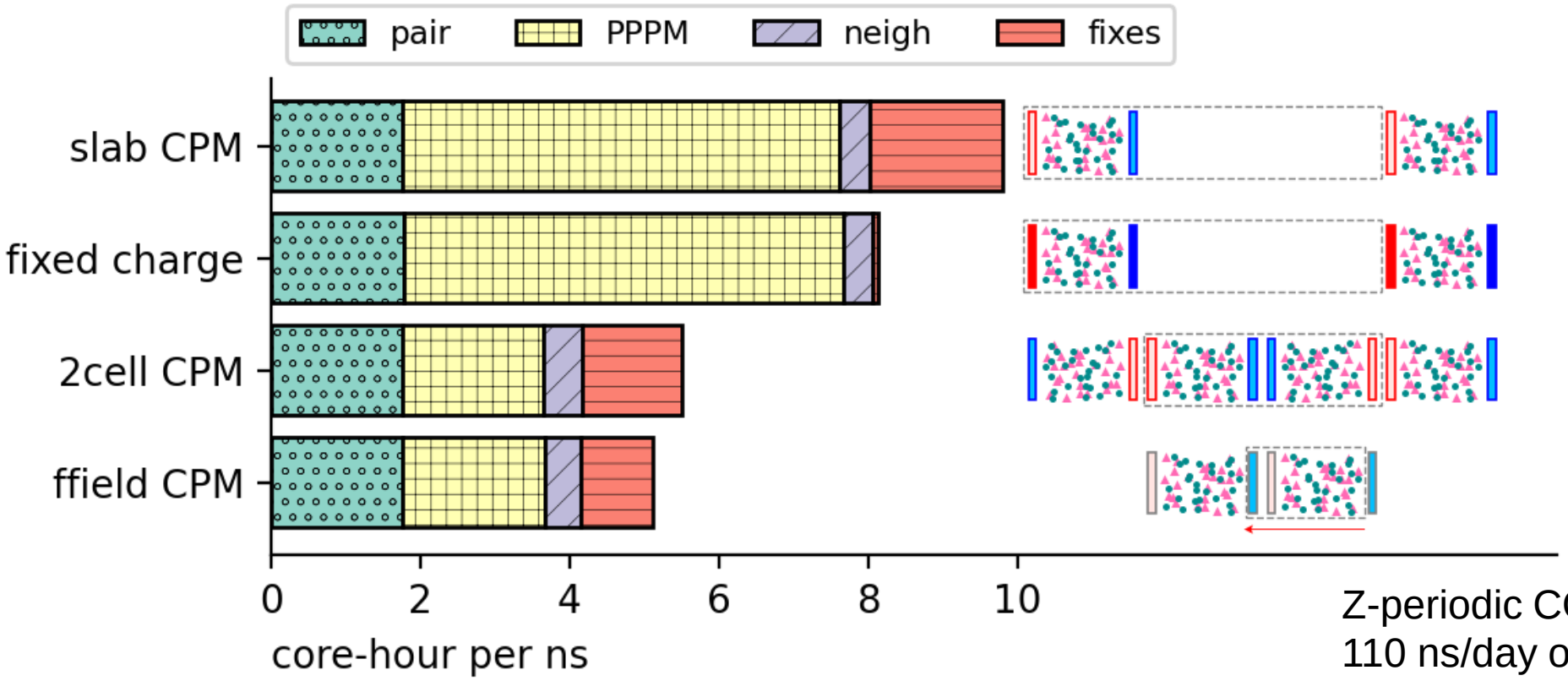
**Full periodicity!**




With slab corrections, kspace is much slower!

Since constant potential forces the electric field outside / between the electrodes to be zero, there are **z-periodic boundary conditions** that allow conp to operate **without kspace_modify slab**.

(c): Dufils et al, PRL **123** (19): 195501 (2019)
(d): Raiteri et al, J Chem Phys **153**: 164714 (2020)




Under some conditions, the savings of avoiding slab mode can even outweigh the overhead of fix conp!

Z-periodic CONP speeds:
110 ns/day on 24 Haswell cores

Box size 32 x 34 x 136 $Å^3$
Electrolyte: IL, 320 ion pairs,
3-site cation + 1-site anion
Electrode: 2x 1 layer conp (768 sites)
+ 2 layer neutral (1536 sites)

# Add secret sauce:

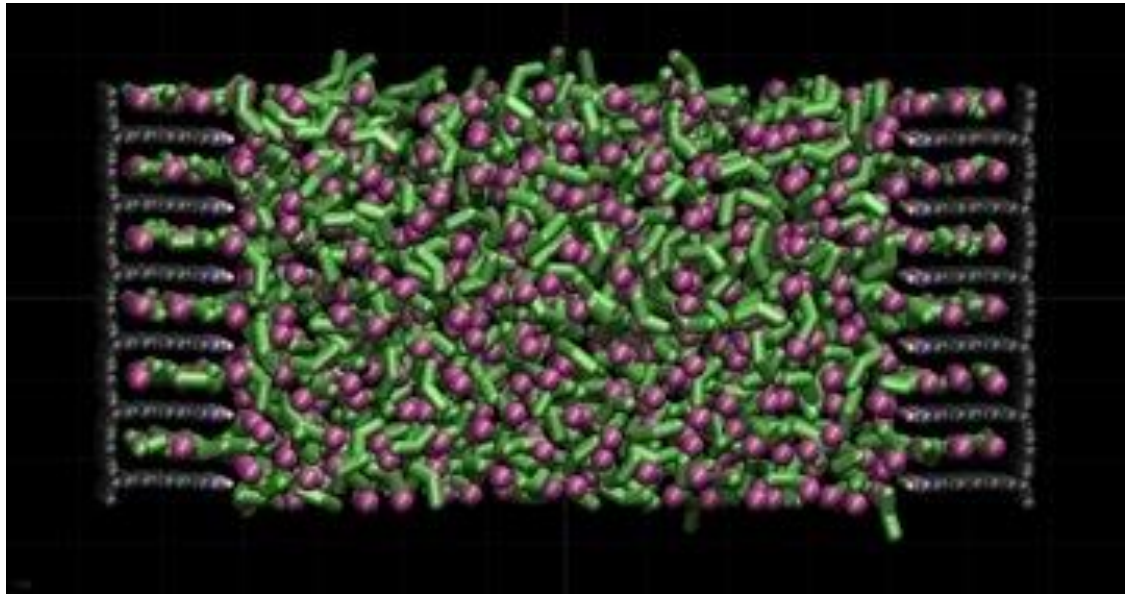
Conp-aware PPPM for even faster runtimes

- `kspace_style pppm/conp` instead of `pppm`
- `fix … conp … pppm`

Seamless integration with USER-INTEL (used in above results)

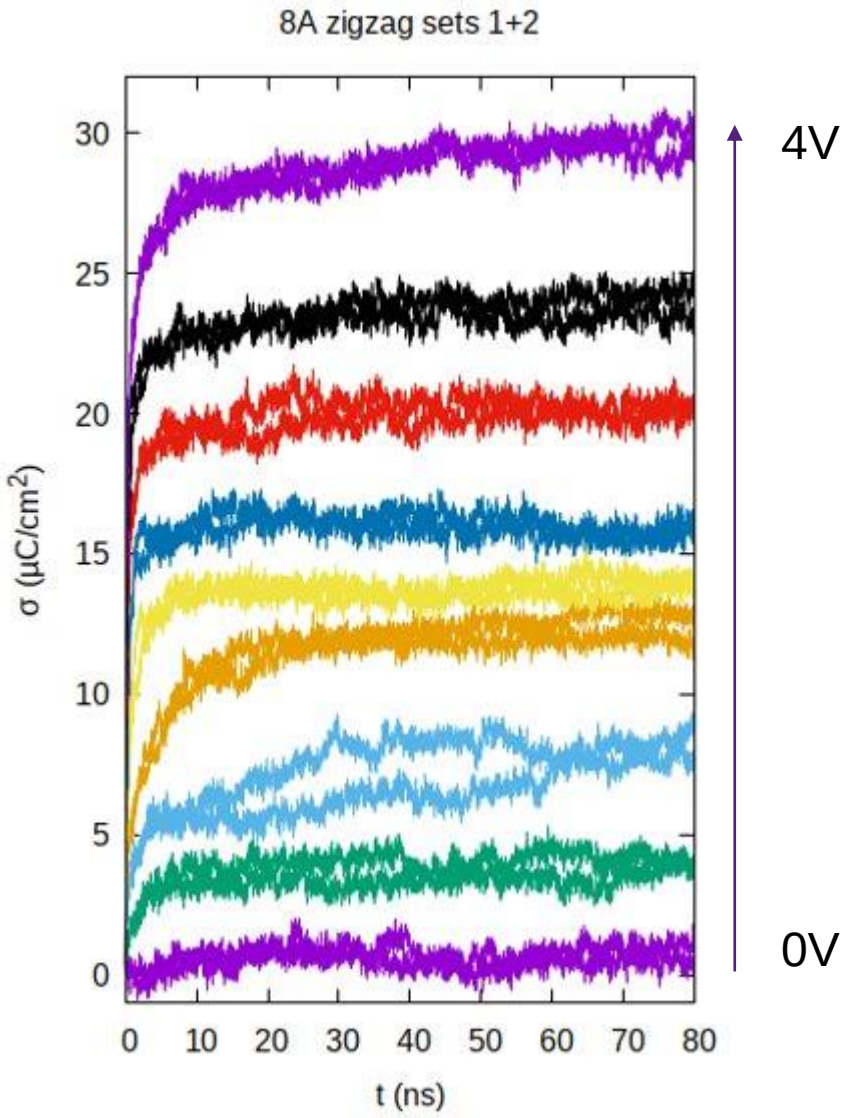
- Follow usual `package / suffix` instructions
- Requires patch of `intel_buffers.h`

# Some Interesting Systems

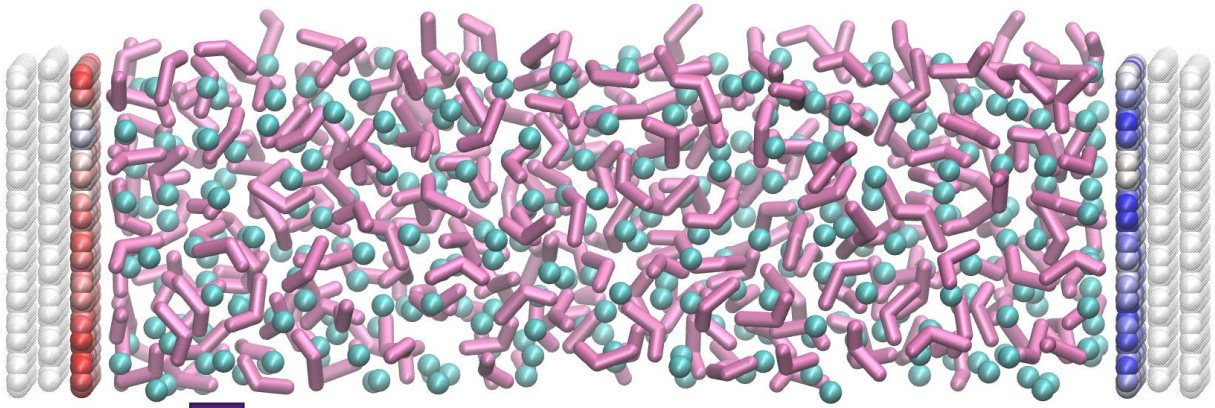


**Graphene nanoribbons – very slow charging and highly variable capacitance!**

Box 39 x 51 x 140 Å$^3$
720 ion pairs (2880 particles total)
+ 2 electrodes (2k sites each)
48-80 ns / day



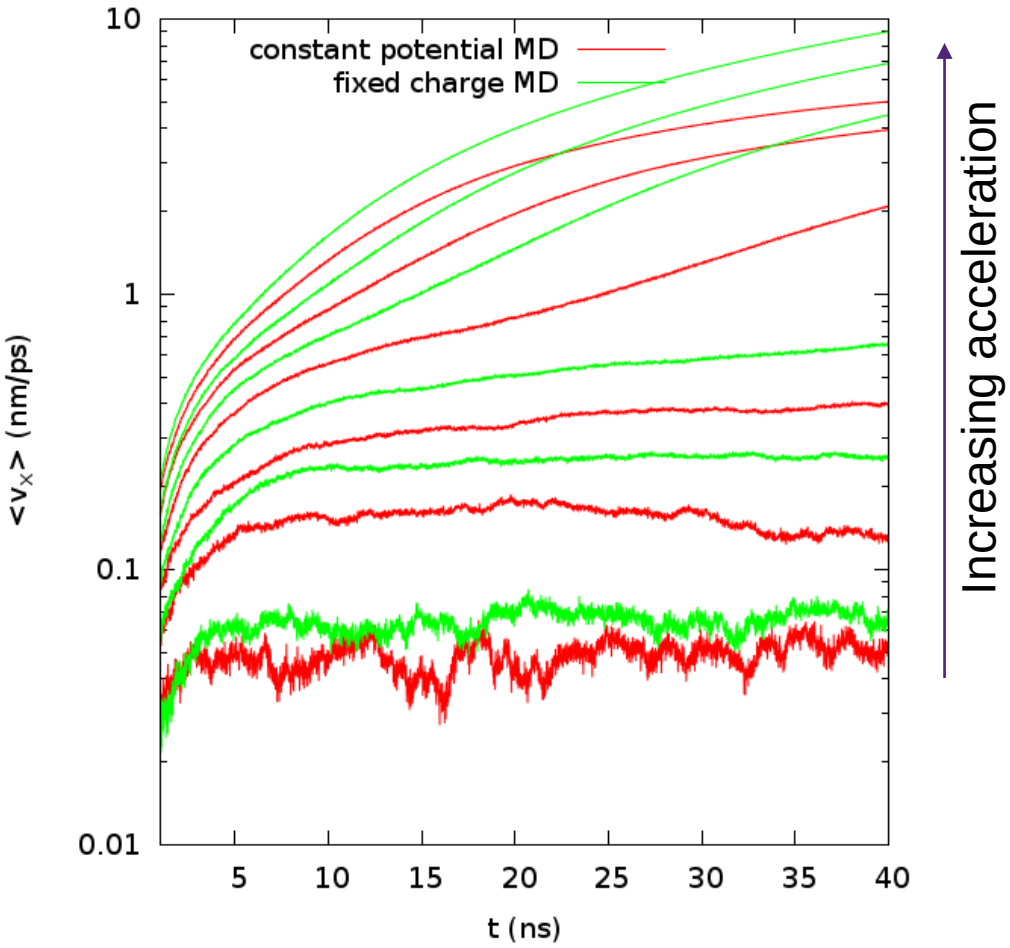
# Some Interesting Systems



“fix gravity” on electrolyte particles – Electrotribology!

CONP shows lower steady velocities / accelerations because of dynamic correlations between electrode charges and electrolyte positions

0V CONP vs fixed (zero) charge electrodes



# What's in the works?

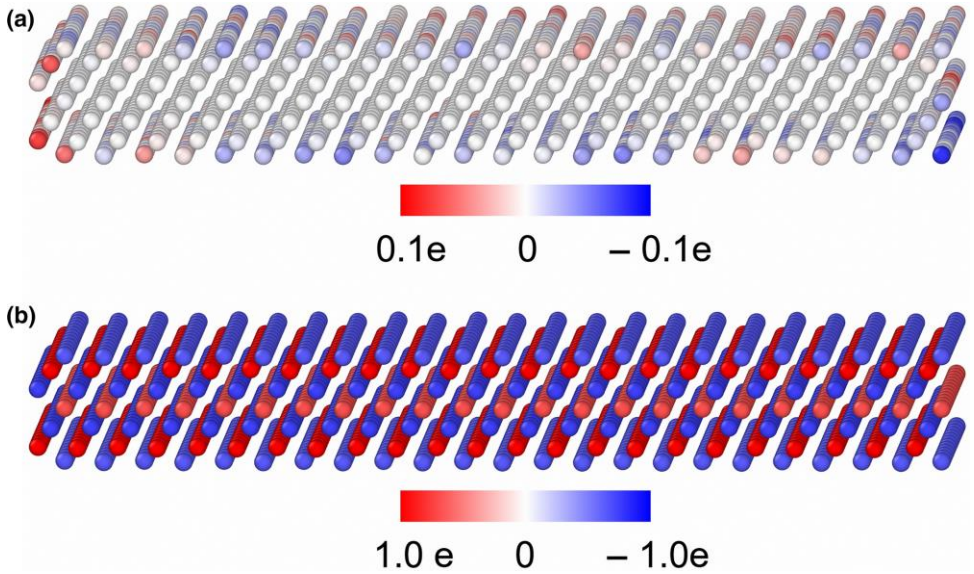
Constant potential method for *heteroatomic conductors* (doped graphene, MOFs, MXenes, TMDs … )

To be *calibrated from DFT calculations*!

(Collab with Prof Peter Cummings @ Vanderbilt,

Dr Paul Kent @ ORNL)

Atomic charges on Mxene electrodes ($Ti_3C_2O_2$) in contact with EMIM-Otf:




CPM: ***Wrong!***

(as compared to DFT)

Xu et al. (2020), Energy Environ. Mater., 3: 235-246.

# Where can I get this?

https://github.com/srtee/lammps-USER-CONP2

# Thank you

Bernhardt Group:
Prof Debra Bernhardt
Dr Emily Kahl
Dr Stephen Sanderson
And my other wonderful colleagues!

Computational resources:

NCI AUSTRALIA
pawsey