Molecular Dynamics with Electron Open-Boundaries

Jarvist Moore Frost, Richard Fogarty, Andrew Horsfield, Tony Paxton

The Hairy Probes[1] formalism for electron open boundaries allows us to apply an electrochemical potential difference across our computational cell within an electronic structure calculation. In the weak-coupling limit (appropriate for electrochemical cells) the method simplifies considerably: the computational effort is essentially the same as for a standard Born-Oppenheimer calculation, while electrons in different parts of the cell can possess different electrochemical potentials.

For large scale molecular dynamics of electrochemical processes, a simplified quantum mechanical description of the electrons is needed. We employ polarisable ion tight-binding which allows for the efficient calculation of electronic structure and forces. We have applied the technique to a simple parallel plate capacitor made from copper[1], and investigated the dynamics of a copper dimer suspended between these plates.

We show that a simple calculation of forces from the out-of-equilibrium electron population gives acceptably energy-conserving dynamics.

We are developing our method to simulate the electrochemistry of corrosion, with molecular dynamics. We are studying the corrosion of magnesium and titanium, as part of a four year research programme between Imperial and King's College London funded by the EPSRC [2].

[1] Mario G. Zauchner, Andrew P. Horsfield, and Tchavdar N. Todorov. Phys. Rev. B 97, 045116 (2018). https://doi.org/10.1103/PhysRevB.97.045116

[2] http://gow.epsrc.ac.uk/NGBOViewGrant.aspx?GrantRef=EP/R005230/1