

# pyscses: a python space-charge site-explicit solver

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## Summary

**pyscses** is an open-source python package for numerical modelling of ionic space-charge regions in crystalline solids. Ionic space-charges are microscopic regions with a local excess or deficiency of charged point defects, giving these regions a net electrostatic charge (Frenkel, 1946). Space-charge regions form at crystallographic interfaces, such as grain boundaries or heterointerfaces between two different materials. The formation of space-charges is due to segregation of charged defects to, or from, these interfaces, and the associated redistribution of defects in adjacent regions of the crystal, due to defect-defect electrostatic interactions (Chiang, Lavik, Kosacki, Tuller, & Ying, 1996; Kim & Maier, 2002; Maier, 1984, 1985, 2003).

The segregation of defects to, or from, space-charge regions can produce local defect concentrations that strongly deviate from the average “bulk” values in a material (Fleig & J., 1996). This can have significant consequences for key material properties. For example, in solid electrolytes, where ionic defects act as mobile charge carriers, space-charge formation at grain boundaries is associated with large changes in ionic conductivity both parallel and perpendicular to the grain boundaries, due to phenomena such as enhanced defect concentrations (Jamnik & Maier, 1999) in grain boundary cores, or reduced defect concentrations in adjacent “depletion” space-charge regions. In the case of solid electrolytes, understanding space-charge formation at grain boundaries and interfaces is a key challenge in developing a theoretical description of the role of crystalline microstructure on macroscopic ion transport (ionic conductivities) (Kim, Fleig, & Maier, 2003).

**pyscses** considers simple one-dimensional models of crystallographic interfaces, and calculates equilibrium defect distributions by solving a modified Poisson-Boltzmann equation (De Souza, Munir, Kim, & Martin, 2011; Maier, 1995). The driving force for defect segregation to or from the interface is described by defect segregation energies, which are defined as

$$\Delta E_{\text{seg}}^{i,x} = E_{\text{f}}^{i,x} - E_{\text{f}}^{i,\infty}$$

where  $E_{\text{f}}^{i,x} = E_{\text{tot}}^{i,\text{lattice}} - E_{\text{tot}}^{\text{lattice}}$ .

## The numerical model

The default model implemented in **pyscses** calculates the equilibrium distribution of point charge defect species distributed on a 1D grid (De Souza et al., 2011; Helgee, Lindman, & Wahnström, 2013; Nyman, Helgee, & Wahnström, 2012; Polfus, Norby, & Bredesen,

2016), with a defect electrochemical potential  $\mu_{i,x}^o$  of

$$\mu_{i,x}^o + RT \ln \left( \frac{c_{i,x}}{1 - c_{i,x}} \right) + z_i F \Phi_x.$$

The  $RT \ln \left( \frac{c_{i,x}}{1 - c_{i,x}} \right)$  term gives the chemical potential for a non-interacting lattice-gas with site exclusion (maximum site occupancy of 1).

Finding the equilibrium distribution of defects is equivalent to solving a modified Poisson-Boltzmann equation, which can be derived by requiring the electrochemical potentials at each site to be equal to a set of reference bulk electrochemical potentials (Maier, 2005).

$$\mu_{i,x}^o + RT \ln \left( \frac{c_{i,x}}{1 - c_{i,x}} \right) + z_i F \Phi_x = \mu_{i,\infty}^o + RT \ln \left( \frac{c_{i,\infty}}{1 - c_{i,\infty}} \right) + z_i F \Phi_\infty,$$

the defect concentrations can be described,

$$c_i = \frac{c_\infty \exp \left( \frac{-z_i \Phi_x + \mu_i}{kT} \right)}{1 + c_\infty \left( \exp \left( \frac{-z_i \Phi_x + \mu_i}{kT} \right) - 1 \right)}.$$

The charge density is proportional to the concentration given by

$$\rho = \sum_i c_i z_i F.$$

The electrostatic potential can be calculated using Poisson's equation,

$$\nabla^2 \Phi = \frac{-\rho}{\epsilon \epsilon_0}.$$

`pyscses` solves this as a second order partial differential equation using a second order finite difference approximation for each site.

`pyscses` can enforce a number of different approximations commonly assumed when space charge formation is considered, including:

- Continuum and site-explicit modelling.
- periodic and Dirichlet boundary conditions.
- “Mott-Schottky” and “Gouy-Champman” conditions (by selecting specific defect species as “fixed”, i.e. immobile).
- Inclusion of site charge for non-defective species.

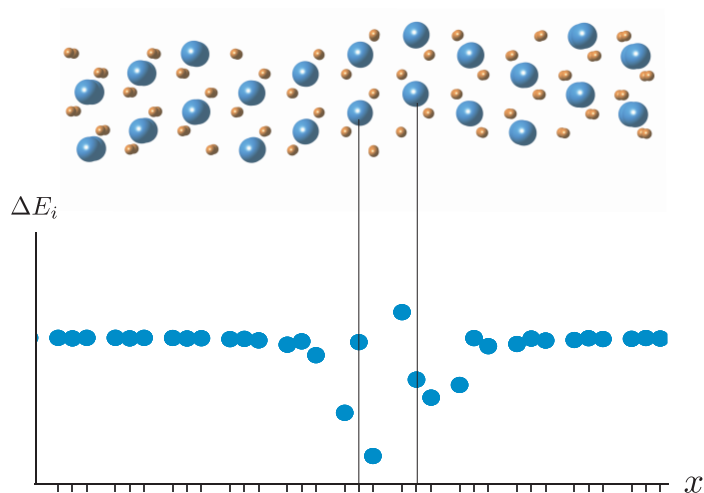
## Typical workflow

To run a standard calculation on a grain boundary, the calculated defect segregation energies and explicit atomic position are projected onto a one-dimensional grid. If the calculation is run using a continuum approximation, the defect segregation energies and atomic positions are interpolated onto a regular grid.

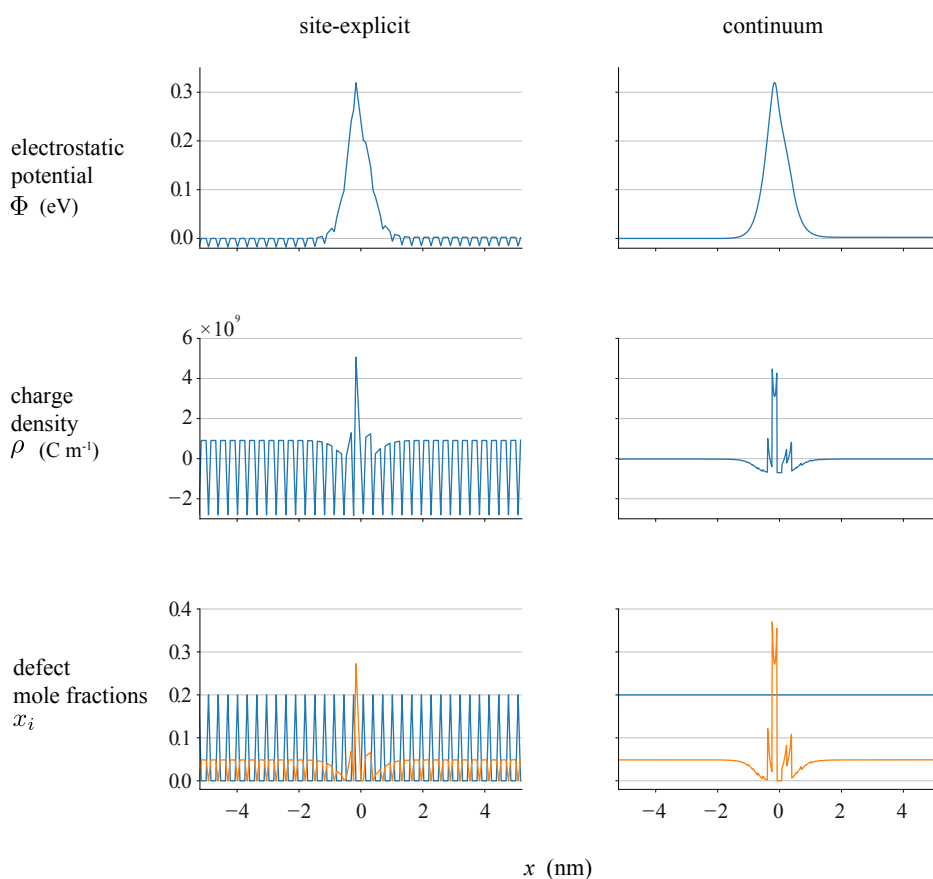
The Poisson-Boltzmann equation is solved self-consistently, giving the electrostatic potential, charge density and defect mole fractions across the space charge region.

## Calculated properties

In addition to allowing calculation of defect, charge, and potential across an interface, `pyscses` can calculate interface (grain boundary) resistivities (Hwang, McLachlan, & Mason, 1999) and activation energies.



**Figure 1:** A crystal structure is generated and the explicit site positions are projected to create a one-dimensional grid. The segregation energy of each defect can then be associated with the appropriate grid point.



**Figure 2:** Example output for Gd-doped ceria. Comparison between the output from the Poisson-Boltzmann solver using continuum and site-explicit modelling

## Grain boundary resistivities

Perpendicular grain boundary resistivities,  $r_{\text{GB}}^{\perp}$ , are calculated by modelling the system as a set of resistors in series:

$$r_{\text{GB}}^{\perp} = \frac{c_{i,\infty} \mu_{i,\infty} z_i}{\sum_i c_{i,x} \mu_{i,x} z_i}.$$

Parallel grain boundary resistivities,  $r_{\text{GB}}^{\parallel}$ , are calculated by modelling the system as a set of resistors in parallel:

$$r_{\text{GB}}^{\parallel} = \frac{1}{\frac{\sum_i c_{i,x} \mu_{i,x} z_i}{c_{i,\infty} \mu_{i,\infty} z_i}}$$

## Activation energies

`pyscses` can be used to calculate the grain boundary contribution to a single defect activation energy by running the Poisson-Boltzmann and resistivity ratio calculations at a range of different temperatures and applying an Arrhenius equation.

$$\ln r_{\text{GB}} = \frac{-E_{\text{act}}}{kT}$$

## Approximations and limitations

- `pyscses` implements a modification of the Poisson-Boltzmann equation, which assumes that defects are non-interacting except for point-charge electrostatics and site exclusion.
- The resistivity and activation energy calculations implemented in `pyscses` assume fixed mobilities for defects.

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