Notes:

- Any of the analysis in [http://web.mit.edu/ceder/publications/prb_76_165435.pdf (http://web.mit.edu/ceder/publications/prb_76_165435.pdf)](http://web.mit.edu/ceder/publications/prb_76_165435.pdf), I should also be able to perform, including prettier diagrams etc. if wanted, just let me know!
- If there is anything else specifically that you would be interested in (such as stuff to do with charge density (see CrystalMaker files), local potential etc., let me know and I can do analysis regarding that.
- These calculations are *in vacuo*, so no specific solvent effects are included. However, the presence of solvent molecules is not expected to significantly influence the equilibrium (relaxed) structures or thermodynamics, but is expected to influence the (crystal growth) kinetics (i.e. enhancing stabilisation of a particular nanoparticle facet). To do more specific investigation on solvent effects etc. would require a huge number of Molecular Dynamics simulations etc. (i.e. beyond the scope of this work). That said, from the predicted surface energies, surface structures, local potential and adsorption site density, a reasonable prediction of solvent stabilisation effects, as a function of solvent dipole moment, (steric) size, dielectric constant etc. may be incurred for each crystal (platelet) face.

Note to self: (Pre-calculations) From looking back at the SEM images in my data, it looks like the platelet side angle is around 45 degrees (101) or (011), or 64 degrees (221) or (021)... Let's try find out...

Structural Relaxation

Many different exchange-correlation functionals trialled for bulk structural relaxation of SnO (see Appendix: Structural Relaxation for results). For all further calculations (surface energy etc.), `optB86b-vdW` was the DFT exchange-correlation functional used, as it accurately incorporates Van der Waal's dispersion effects (important for layered materials obvs)(see [https://doi.org/10.1039/C7CP00284J (https://doi.org/10.1039/C7CP00284J)](https://doi.org/10.1039/C7CP00284J), [https://doi.org/10.1103/PhysRevMaterials.2.034005 (https://doi.org/10.1103/PhysRevMaterials.2.034005)](https://doi.org/10.1103/PhysRevMaterials.2.034005)), with a mean relative error of c. 0.5% for the interlayer spacing in layered solids ([https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.3.063602 (https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.3.063602)](https://journals.aps.org/prmaterials/abstract/10.1103/PhysRevMaterials.3.063602)).

Relaxing from the initial Materials Project structure for SnO, the following results were obtained:

optB86b-vdW: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$

a = 3.832, *b* = 3.832, *c* = 4.793, α = 90, β = 90, γ = 90

In [16]:
```
from pymatgen.core.surface import SlabGenerator, generate_all_slabs
, Structure, Lattice
import pymatgen.symmetry.analyzer as pmgsyman
```

In [17]:
```
optB86bvdW_relaxed = Structure.from_file("VASP_Files/optB86b-vdW/CO
NTCAR")
optB86bvdW_relaxed.add_oxidation_state_by_guess()
```

Relaxed (predicted) structural parameters:

In [18]:
```
optB86bvdW_relaxed
```

Out[18]:
```
Structure Summary
Lattice
    abc : 3.8321500113692926 3.8321500113692926 4.792723931047374
 angles : 90.0 90.0 90.0
 volume : 70.3829420145544
      A : 3.8321500113692926 -0.0 0.0
      B : -1e-16 3.8321500113692926 0.0
      C : -0.0 0.0 4.792723931047374
PeriodicSite: Sn2+ (2.8741, 2.8741, 1.1614) [0.7500, 0.7500, 0.242
3]
PeriodicSite: Sn2+ (0.9580, 0.9580, 3.6313) [0.2500, 0.2500, 0.757
7]
PeriodicSite: O2- (0.9580, 2.8741, 0.0000) [0.2500, 0.7500, 0.0000
]
PeriodicSite: O2- (2.8741, 0.9580, 0.0000) [0.7500, 0.2500, 0.0000
]
```

In [19]:
```
spganalyse_opt = pmgsyman.SpacegroupAnalyzer(optB86bvdW_relaxed)
```

In [20]:
```
print("Point group symbol, space group symbol, space group number:"
)
print(spganalyse_opt.get_point_group_symbol(), '\t\t\t', spganalyse
_opt.get_space_group_symbol(),
      '\t\t\t', spganalyse_opt.get_space_group_number())
```

```
Point group symbol, space group symbol, space group number:
4/mmm                        P4/nmm                         129
```

Maintains the same initial symmetry (P4/nmm), and does not relax to a different structure, as expected.

Experimental:

(ICSD 11516) a,b,c = 3.799, 3.799, 4.841

(ICSD 16481) a,b,c = 3.803, 3.803, 4.838

In [21]:
```
print("Taking a,b = 3.80 Angstrom, c = 4.84 Angstrom as the experim
ental lattice parameters")
print("with a,b = 3.832, c = 4.793 as the calculated parameters, th
e relative error in")
print(f"a,b is {0.032/3.8:.2%}, and {(4.84-4.793)/4.84:.2%} for c")
```

```
Taking a,b = 3.80 Angstrom, c = 4.84 Angstrom as the experimental
lattice parameters
with a,b = 3.832, c = 4.793 as the calculated parameters, the rela
tive error in
a,b is 0.84%, and 0.97% for c
```

Less than 1% error in predicted lattice parameters = good agreement with experiment.
Also, note that the DFT calculations are athermal (i.e. at T = 0K), so a slight expansion along the *c* direction would be expected (i.e. we would expect the predicted *c* lattice parameter to be *smaller* than the experimental value, as is the case.

Slab Calculations

In [39]:
```
optB86bvdW_slabs_vacthic_10 = generate_all_slabs(optB86bvdW_relaxed
, max_index=2,
                                                  min_slab_size=10,
min_vacuum_size=10, lll_reduce=True)
```

In [40]:
```
dipole_free_slabs_vacthic_10 = []
for slab in optB86bvdW_slabs_vacthic_10:
    if not slab.is_polar():
        dipole_free_slabs_vacthic_10.append(slab)
```

In [9]:
```
#from pymatgen.entries.computed_entries import ComputedStructureEnt
ry
from pymatgen.io.vasp.outputs import Vasprun
bulk_sno_vasprun = Vasprun("./VASP_Files/optB86b-vdW/bulk_rerun/vas
prun.xml")
bulk_sno_entry = bulk_sno_vasprun.get_computed_entry()
```

In [10]:
```
import scipy.constants as scpc
import os
```

In [11]:
```
from pymatgen.io.vasp.outputs import Vasprun
from pymatgen.analysis.surface_analysis import SlabEntry
dipolefree_slabs_vaspruns = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/"):
    for name in files:
        if "_Slab" in root[-10:]:
            if "vasprun" in name:
                #print(os.path.join(root, name))
                dipolefree_slabs_vaspruns[root[-8:]] = {'vasprun':
Vasprun(os.path.join(root, name)),
                                                         'thickness'
: 10, 'vacuum': 10,
                                                         'miller ind
ex': (int(root[-8]), int(root[-7]), int(root[-6]))}

for k, v in dipolefree_slabs_vaspruns.items():
    v['final_energy'] = v['vasprun'].final_energy
    v['SlabEntry'] = SlabEntry.from_computed_structure_entry(v['vas
prun'].get_computed_entry(),
                                                             v['mil
ler index'])
    v['SurfaceEnergyJm2'] = v['SlabEntry'].surface_energy(
        bulk_sno_entry)*scpc.electron_volt*10**20  # Convert eV/A^2
to J/m^2
```

In [12]:
```
for k, v in dipolefree_slabs_vaspruns.items():
    print(
        f"Miller Index: {v['miller index']} \t Surface Energy:   {v
['SurfaceEnergyJm2']:.2f} J/m^2")
```

```
Miller Index: (2, 1, 2)         Surface Energy:   0.64 J/m^2
Miller Index: (1, 0, 1)         Surface Energy:   0.57 J/m^2
Miller Index: (1, 0, 0)         Surface Energy:   0.61 J/m^2
Miller Index: (1, 1, 1)         Surface Energy:   0.71 J/m^2
Miller Index: (0, 0, 1)         Surface Energy:   0.25 J/m^2
Miller Index: (2, 2, 1)         Surface Energy:   1.30 J/m^2
Miller Index: (2, 0, 1)         Surface Energy:   0.61 J/m^2
Miller Index: (1, 1, 2)         Surface Energy:   0.61 J/m^2
Miller Index: (2, 1, 0)         Surface Energy:   0.77 J/m^2
Miller Index: (2, 1, 1)         Surface Energy:   1.14 J/m^2
Miller Index: (1, 0, 2)         Surface Energy:   0.48 J/m^2
```

In [13]:
```
from pymatgen.analysis.wulff import WulffShape
```

In [22]:
```
sno_miller_indices = []
sno_surface_energies_jm2 = []
for k, v in dipolefree_slabs_vaspruns.items():
    if v['miller index'] in [(0, 0, 1)]:
        # Bug in the code, can't use 001 miller index, need to
        c_energy = v['SurfaceEnergyJm2']
        # specify as 0.0000000000001, 0, 1
    else:
        #  Might need to reformat this
        sno_miller_indices.append(v['miller index'])
        sno_surface_energies_jm2.append(v['SurfaceEnergyJm2'])
# Bug in the code, can't use 001 miller index,
sno_miller_indices.append((0.00000000001, 0, 1))
# need to specify as 0.0000000000001, 0, 1
sno_surface_energies_jm2.append(c_energy)
wulff_sno = WulffShape(optB86bvdW_relaxed.lattice,
                       sno_miller_indices, sno_surface_energies_jm2
)
```

In [23]:
```
print(f"Miller Index:  Normalised Surface Area in Wulff Shape: (i.e
. Wulff surface area fraction)")
for k, v in wulff_sno.miller_area_dict.items():
    print(k, f"\t\t\t {v/wulff_sno.surface_area:.3f}")
print("\n'(1e-11, 0, 1)' = (0, 0, 1) btw")
```

```
Miller Index:  Normalised Surface Area in Wulff Shape: (i.e. Wulff
surface area fraction)
(2, 1, 2)                        0.160
(1, 0, 1)                        0.111
(1, 0, 0)                        0.205
(1, 1, 1)                        0.002
(2, 2, 1)                        0.000
(2, 0, 1)                        0.032
(1, 1, 2)                        0.001
(2, 1, 0)                        0.006
(2, 1, 1)                        0.000
(1, 0, 2)                        0.047
(1e-11, 0, 1)                    0.437

'(1e-11, 0, 1)' = (0, 0, 1) btw
```

In [24]:
```
print("Shape factor: %.3f, Anisotropy: \
%.3f, Weighted surface energy: %.3f J/m^2" % (wulff_sno.shape_facto
r,
                                                 wulff_sno.anisotro
py,
                                                 wulff_sno.weighted
_surface_energy))
# Typically in the literature when discussing surface anisotropy, w
e would only look at the ratios of
# 2 surface energies when talking about anisotropy. eg. the ratio o
f a generic fcc (111) to (100)
# surface energy should be less than 1 as the (111) facet is the cl
osest packed surface of an fcc
# structure and should have the lowest surface energy. However this
method of determining surface
# anisotropy does not allow us to determine an overall anisotropy o
f a material, ie. how different
# are all the surface energies for a material. As such, we used the
Coefficient of Variation from the
# weighted surface energy. For reference, an ideal sphere Wulff sha
pe (eg. completely isotropic) has
# a anisotropy of 0.
# shape_factor:
# An alternative to anisotropy. This is useful for determining the
critical nucleus size. A
# large shape factor indicates great anisotropy. See Ballufi, R. W.
, Allen, S. M. & Carter,
# W. C. Kinetics of Materials. (John Wiley & Sons, 2005), p.461
```

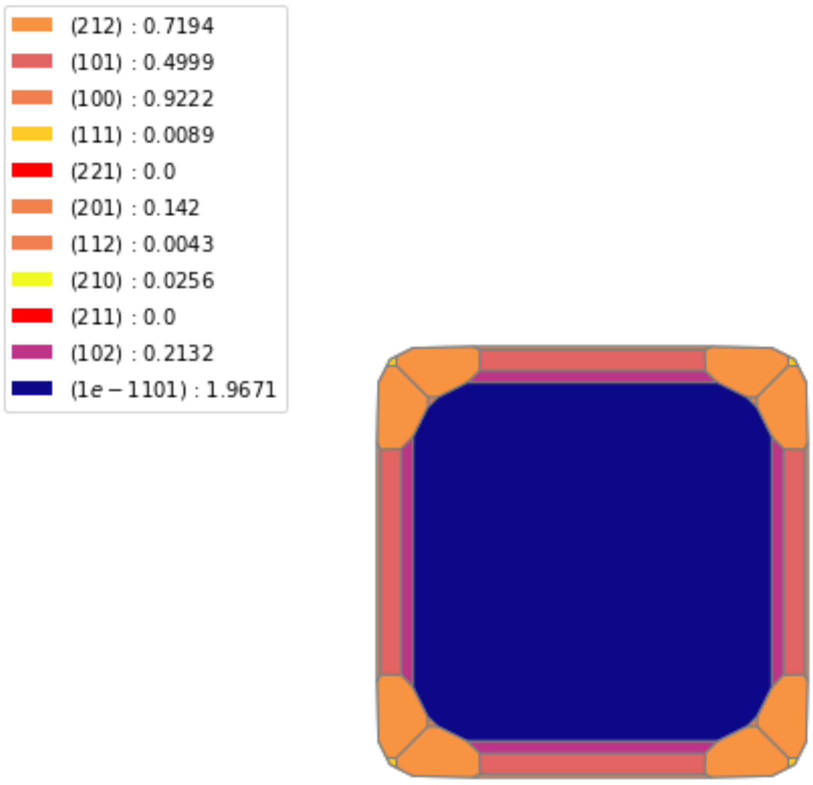
```
Shape factor: 5.853, Anisotropy: 0.391, Weighted surface energy: 0
.450 J/m^2
```

weighted_surface_energy:

Surface Gibbs free energy for a crystal is given by $\Delta G = \sum_{hkl} \gamma_{hkl} A_{hkl}$. Where γ_{hkl} is the surface energy of facet (hkl) and A_{hkl} is the surface area of that particular facet that occupies the Wulff shape. We can normalize this value with the total surface area of the Wulff shape to get the weighted (average) surface energy for a particular material $\bar{\gamma} = \frac{\Delta G}{\sum_{hkl} A_{hkl}}$

In [31]:
```
%load_ext autoreload
%autoreload 2
%matplotlib inline
wulff_plot = wulff_sno.get_plot(
    color_set='plasma', grid_off=False, show_area=True)
```

```
The autoreload extension is already loaded. To reload it, use:
  %reload_ext autoreload
```



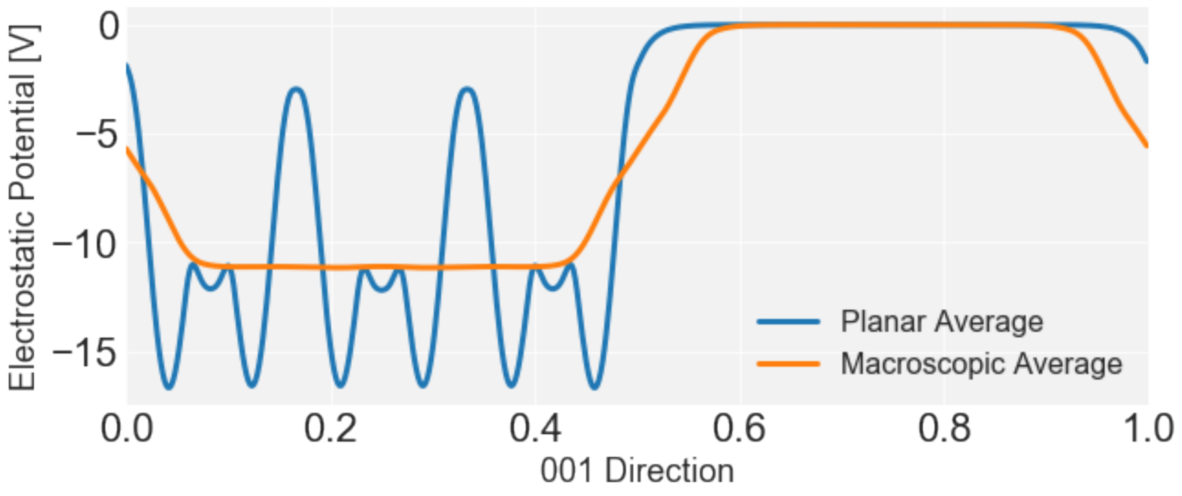
See images and videos for different viewpoints on Wulff Shape. Looks similar to the platelets in the Ethylene Glycol solvent. Suggests that solvents (like H_2O and EtOH) have strong kinetic effects, further stabilising the 001 face relative to other surfaces (-> making thinnner platelets).

In particular, if you look at the CrystalMaker `Surface_Relaxation` file, which shows the initial and final (relaxed) structures for the important crystal facets ((001), (100), (101) and (212) - see Labelled Wulff Shape). Notably, even after surface relaxations (very small for (001) as expected, but some small reconstructions for the others), only the (001) surface has exposed Tin atoms (in all other cases, Oxygen is more prominent at the surface). Hence more amenable to adsorption via Oxygen in H_2O, EtOH etc. Particularly for H_2O -> close-packed adsorption on (001) surface, strong kinetic stabilisation, wide squares?

In [1]:
```
import macrodensity as md
import io
import sys
import matplotlib.pyplot as plt
import matplotlib as mpl
```

In [100]:
```
import numpy as np
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/001_Slab/LOCPOT'
lattice_vector = (4.8)
output_file = 'whofuckingcares.dat'
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(
    input_file, quiet=True)  # execute our now mute functions
vector_a, vector_b, vector_c, av, bv, cv = md.matrix_2_abc(Lattice)
resolution_x = vector_a/NGX
resolution_y = vector_b/NGY
resolution_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot, NGX, NGY, NGZ)
planar001 = md.planar_average(grid_pot, NGX, NGY, NGZ)
macro = md.macroscopic_average(planar001, lattice_vector, resolutio
n_z)
fig, ax = plt.subplots(1, 1, sharex=True, figsize=(10, 4))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0, 1, 1.0/len(planar001)), planar001 -
        macro[int(3*length/4)], label="Planar Average", lw=3)
ax.plot(np.arange(0, 1, 1.0/len(planar001)), macro -
        macro[int(3*length/4)], label="Macroscopic Average", lw=3)
plt.setp(ax, xlim=(0, 1), facecolor=((0.95, 0.95, 0.95)))
ax.grid(True)
ax.legend(fontsize=16)
ax.set_ylabel('Electrostatic Potential [V]', fontsize=18)
ax.set_xlabel('001 Direction', fontsize=18)
plt.show()
length = len(macro)
offset = np.mean(macro[int(length/4 - length/8):int(length/4 + leng
th/8)]) - macro[int(3*length/4)]
print(f"Using plateaus in the centre of each region: Offset = "
      f"{offset:.4f} V")
```

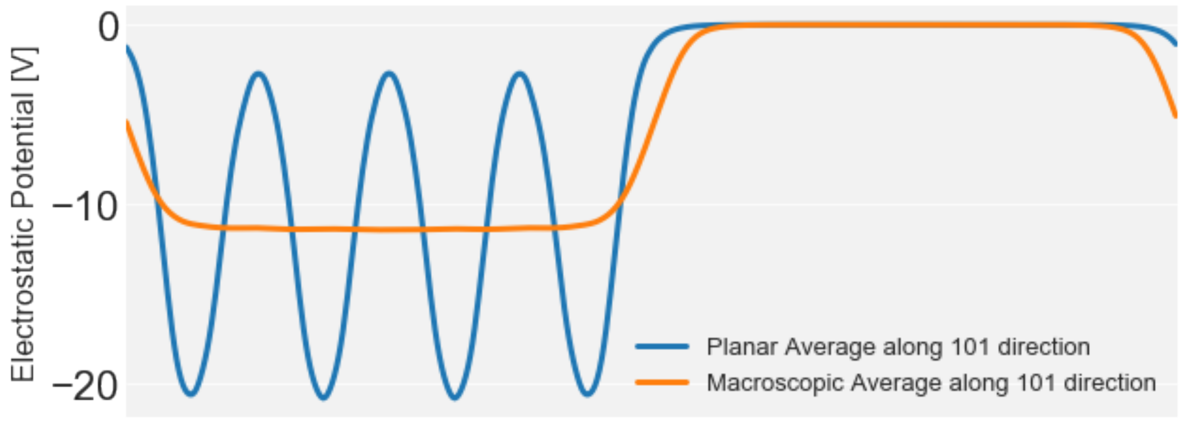
```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  2.3021584638627245e-13
```



```
Using plateaus in the centre of each region: Offset = -11.1349 V
```

In [99]:
```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/101_Slab/LOCPOT'
lattice_vector = (3)
output_file = 'whofuckingcares.dat'
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(
    input_file, quiet=True)  # execute our now mute functions
vector_a, vector_b, vector_c, av, bv, cv = md.matrix_2_abc(Lattice)
resolution_x = vector_a/NGX
resolution_y = vector_b/NGY
resolution_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot, NGX, NGY, NGZ)
planar = md.planar_average(grid_pot, NGX, NGY, NGZ)
macro = md.macroscopic_average(planar, lattice_vector, resolution_z
)
fig, ax = plt.subplots(1, 1, sharex=True, figsize=(10, 4))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0, 1, 1.0/len(planar)), planar -
        macro[int(3*length/4)], label="Planar Average along 101 dir
ection", lw=3)
ax.plot(np.arange(0, 1, 1.0/len(planar)), macro -
        macro[int(3*length/4)], label="Macroscopic Average along 10
1 direction", lw=3)
plt.setp(ax, xlim=(0, 1), facecolor=((0.95, 0.95, 0.95)))
ax.grid(True)
ax.legend(fontsize=13)
ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
ax.set_xlabel('101 Direction', fontsize=18)
ax.get_xaxis().set_visible(False)
plt.show()
length = len(macro)
offset = np.mean(macro[int(length/4 - length/8):int(length/4 + leng
th/8)]) - macro[int(3*length/4)]
print(f"Using plateaus in the centre of each region: Offset = "
      f"{offset:.4f} V")
```

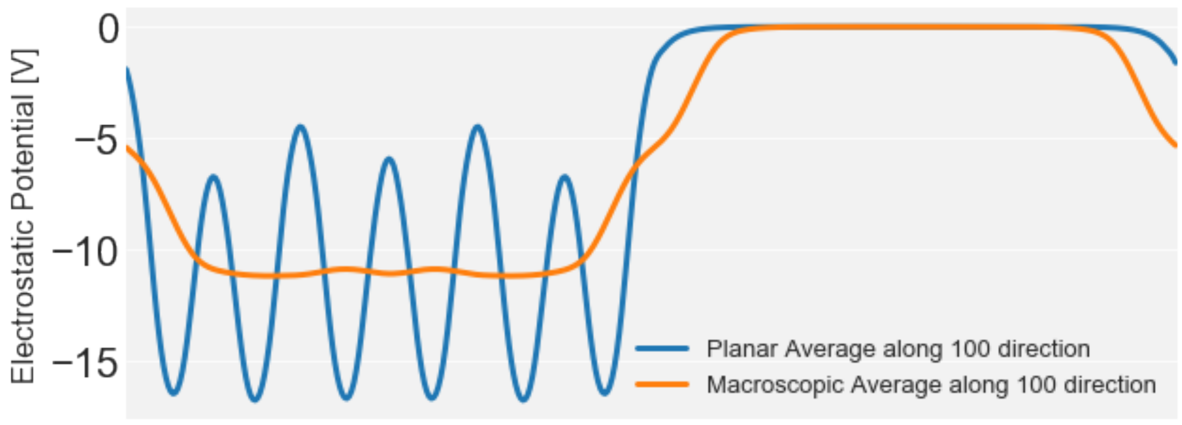
```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  5.684341886080802e-15
```



```
Using plateaus in the centre of each region: Offset = -11.4181 V
```

In [98]:
```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/100_Slab/LOCPOT'
lattice_vector = (3.83)
output_file = 'whofuckingcares.dat'
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(
    input_file, quiet=True)  # execute our now mute functions
vector_a, vector_b, vector_c, av, bv, cv = md.matrix_2_abc(Lattice)
resolution_x = vector_a/NGX
resolution_y = vector_b/NGY
resolution_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot, NGX, NGY, NGZ)
planar = md.planar_average(grid_pot, NGX, NGY, NGZ)
macro = md.macroscopic_average(planar, lattice_vector, resolution_z
)
fig, ax = plt.subplots(1, 1, sharex=True, figsize=(10, 4))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0, 1, 1.0/len(planar)), planar -
        macro[int(3*length/4)], label="Planar Average along 100 dir
ection", lw=3)
ax.plot(np.arange(0, 1, 1.0/len(planar)), macro -
        macro[int(3*length/4)], label="Macroscopic Average along 10
0 direction", lw=3)
plt.setp(ax, xlim=(0, 1), facecolor=((0.95, 0.95, 0.95)))
ax.grid(True)
ax.legend(fontsize=13)
ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
ax.set_xlabel('100 Direction', fontsize=18)
ax.get_xaxis().set_visible(False)
plt.show()
length = len(macro)
offset = np.mean(macro[int(length/4 - length/8):int(length/4 + leng
th/8)]) - macro[int(3*length/4)]
print(f"Using plateaus in the centre of each region: Offset = "
      f"{offset:.4f} V")
```

```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.1165671561944431e-14
```

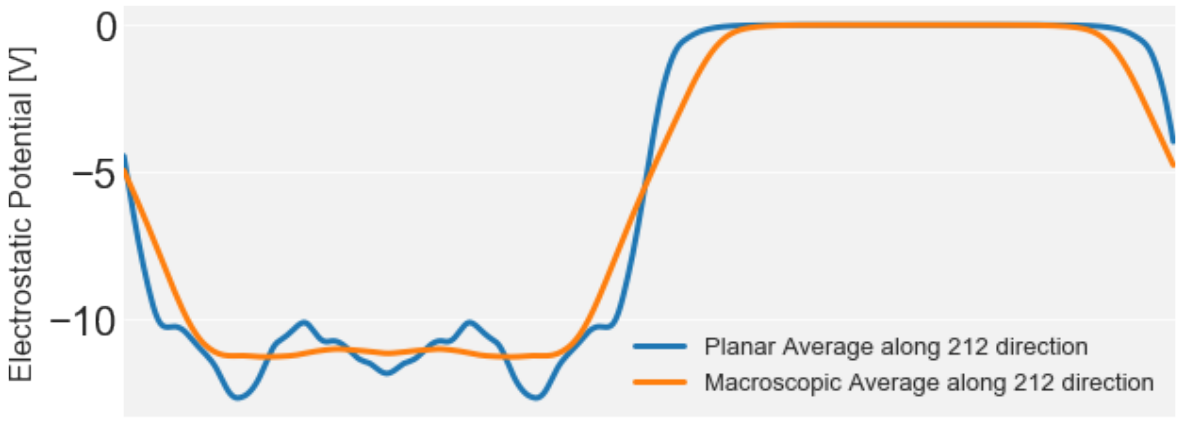


```
Using plateaus in the centre of each region: Offset = -11.0539 V
```

In [96]:

```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/212_Slab/LOCPOT'
lattice_vector = (3)
output_file = 'whofuckingcares.dat'
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(
    input_file, quiet=True)  # execute our now mute functions
vector_a, vector_b, vector_c, av, bv, cv = md.matrix_2_abc(Lattice)
resolution_x = vector_a/NGX
resolution_y = vector_b/NGY
resolution_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot, NGX, NGY, NGZ)
planar = md.planar_average(grid_pot, NGX, NGY, NGZ)
macro = md.macroscopic_average(planar, lattice_vector, resolution_z
)
fig, ax = plt.subplots(1, 1, sharex=True, figsize=(10, 4))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0, 1, 1.0/len(planar)), planar -
        macro[int(3*length/4)], label="Planar Average along 212 dir
ection", lw=3)
ax.plot(np.arange(0, 1, 1.0/len(planar)), macro -
        macro[int(3*length/4)], label="Macroscopic Average along 21
2 direction", lw=3)
plt.setp(ax, xlim=(0, 1), facecolor=((0.95, 0.95, 0.95)))
ax.grid(True)
ax.legend(fontsize=13)
ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
ax.set_xlabel('212 Direction', fontsize=18)
ax.get_xaxis().set_visible(False)
plt.show()
length = len(macro)
offset = np.mean(macro[int(length/4 - length/8):int(length/4 + leng
th/8)]) - macro[int(3*length/4)]
print(f"Using plateaus in the centre of each region: Offset = "
      f"{offset:.4f} V")
```

```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  3.684295666904223e-15
```



```
Using plateaus in the centre of each region: Offset = -11.1611 V
```

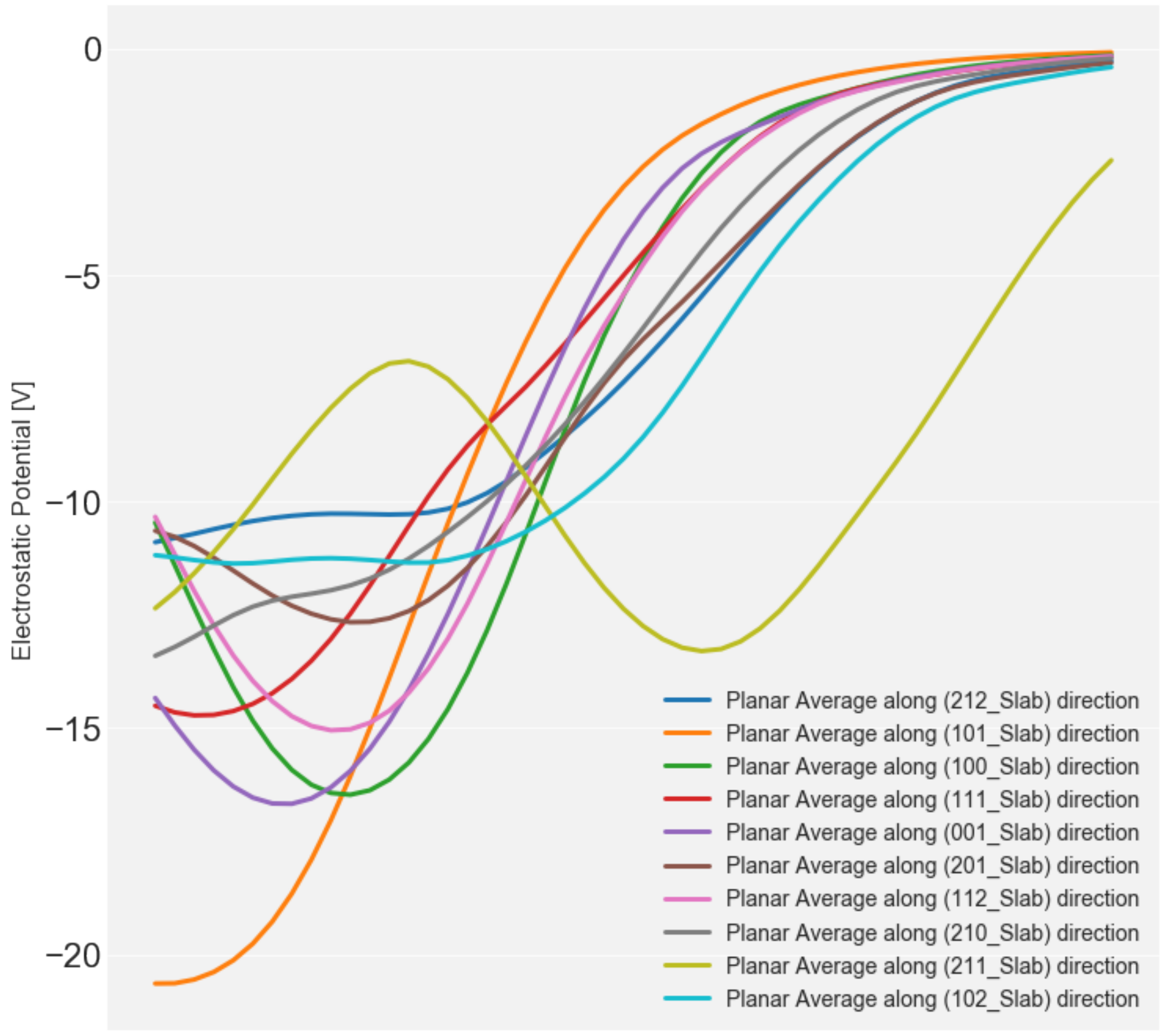
See Appendix: Local Potential Plots for other surfaces, if of interest.

Plot of Electrostatic Potential at Relaxed Surface Edge, for all terminations:

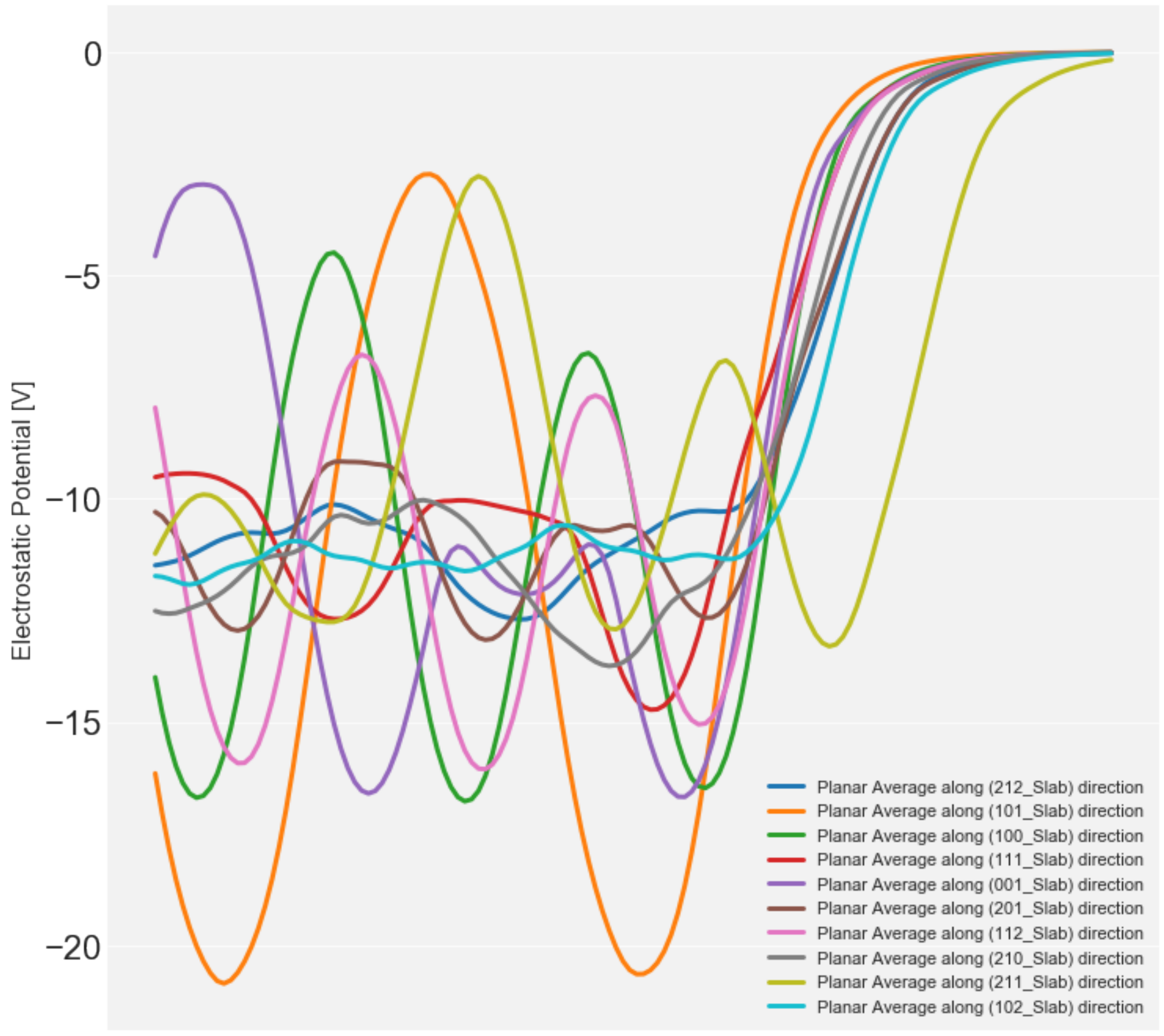
In [46]:
```
import os
planar_data = {}
macro_data = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/"):
    for name in files:
        if "_Slab" in root[-10:]:
            if "LOCPOT" == name:
                if "221" in root:
                    continue
                input_file = os.path.join(root, name)
                lattice_vector = (4.8)
                output_file = 'whofuckingcares.dat'
                vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_den
sity(
                    input_file, quiet=True)  # execute our now mute
functions
                vector_a, vector_b, vector_c, av, bv, cv = md.matri
x_2_abc(
                    Lattice)
                resolution_x = vector_a/NGX
                resolution_y = vector_b/NGY
                resolution_z = vector_c/NGZ
                grid_pot, electrons = md.density_2_grid(
                    vasp_pot, NGX, NGY, NGZ)
                planar_data[root[-8:]
                            ] = md.planar_average(grid_pot, NGX, NG
Y, NGZ)
                macro_data[root[-8:]] = md.macroscopic_average(
                    planar_data[root[-8:]], lattice_vector, resolut
ion_z)
```

```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  3.684295666904223e-15
Reading header information...
Reading 3D data using Pandas...
Average of the average =  6.158037043254202e-15
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.1419436824715896e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  5.921189464667502e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  2.3021584638627245e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -2.590435802371108e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.597029387041749e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  1.5370924487871556e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  1.2823875294998287e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.8947806286936005e-15
```

In [47]:
```
%matplotlib inline
fig, ax = plt.subplots(1, 1, figsize=(12, 12))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
for i, k in enumerate(planar_data):
    half = int(len(planar_data[k])/2)
    ax.plot((planar_data[k]-planar_data[k][350])[half-30:half+20],
            label=f"Planar Average along ({k}) direction", lw=3)
    ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
    ax.get_xaxis().set_visible(False)
    ax.grid(True)
    ax.legend(fontsize=14)
plt.setp(ax, facecolor=((0.95, 0.95, 0.95)))
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

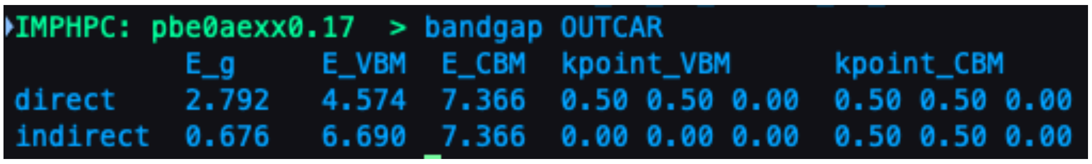


```
In [50]: %matplotlib inline
         fig, ax = plt.subplots(1, 1, figsize=(12, 12))
         textsize = 22
         mpl.rcParams['xtick.labelsize'] = textsize
         mpl.rcParams['ytick.labelsize'] = textsize
         plt.rcParams['legend.title_fontsize'] = 22
         for i, k in enumerate(planar_data):
             half = int(len(planar_data[k])/2)
             ax.plot((planar_data[k]-planar_data[k][350])[half-100:half+40],
                     label=f"Planar Average along ({k}) direction", lw=3)
             ax.set_ylabel('Electrostatic Potential [V]', fontsize=16)
             ax.get_xaxis().set_visible(False)
             ax.grid(True)
             ax.legend(fontsize=11)
         plt.setp(ax, facecolor=((0.95, 0.95, 0.95)))
         plt.show()
         #print(f"Using plateaus in the centre of each slab: Offset (Bi rela
         tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

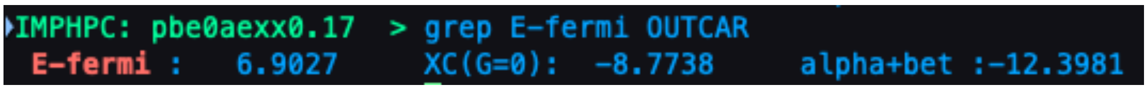


Work Function, Ionisation Potential and Electron Affinity

Hybrid DFT was used to give an accurate description of the electronic structure, for which vanilla GGA DFT has several well-known shortcomings. See https://pubs-rsc-org.libproxy.ucl.ac.uk/en/content/articlelanding/2013/TC/c3tc31863j (https://pubs-rsc-org.libproxy.ucl.ac.uk/en/content/articlelanding/2013/TC/c3tc31863j) (Scanlon & Watson paper) for comparisons. Specifically, a modified PBE0 hybrid DFT functional, with 17% exact Hartree-Fock exchange, was used, to give an indirect bandgap of 0.68 eV, in agreement with the experimental value of ~ 0.7 eV. With this functional, the direct gap is calculated as 2.79 eV, in close agreement with the experimental value of 2.6 - 2.8 eV.



```
IMPHPC: pbe0aexx0.17  > bandgap OUTCAR
            E_g      E_VBM   E_CBM   kpoint_VBM        kpoint_CBM
direct     2.792    4.574   7.366   0.50 0.50 0.00    0.50 0.50 0.00
indirect   0.676    6.690   7.366   0.00 0.00 0.00    0.50 0.50 0.00
```



```
IMPHPC: pbe0aexx0.17  > grep E-fermi OUTCAR
 E-fermi :   6.9027     XC(G=0):  -8.7738     alpha+bet :-12.3981
```

In [12]:
```
import numpy as np
```

In [10]:
```python
vbm = 6.690
cbm = 7.366
fermi = 6.9027
electrostatic_offsets = {'001': -11.1349, '101': -
                         11.4181, '100': -11.0539, '212': -11.1611}
ionisation_potentials = {}
electron_affinities = {}
work_functions = {}
for key, val in electrostatic_offsets.items():
    ionisation_potentials[key] = vbm + val
    electron_affinities[key] = cbm + val
    work_functions[key] = fermi + val
print("Ionisation Potentials: (i.e. VBM wrt Vacuum)")
for k,v in ionisation_potentials.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
print("\nElectron Affinities: (i.e. CBM wrt Vacuum)")
for k,v in electron_affinities.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
print("\nWork Functions: (i.e. Fermi Level wrt Vacuum)")
for k,v in work_functions.items():
    print(f"Surface Orientation: {k} -> {v:.2f} V")
```

```
Ionisation Potentials: (i.e. VBM wrt Vacuum)
Surface Orientation: 001 -> -4.44 V
Surface Orientation: 101 -> -4.73 V
Surface Orientation: 100 -> -4.36 V
Surface Orientation: 212 -> -4.47 V

Electron Affinities: (i.e. CBM wrt Vacuum)
Surface Orientation: 001 -> -3.77 V
Surface Orientation: 101 -> -4.05 V
Surface Orientation: 100 -> -3.69 V
Surface Orientation: 212 -> -3.80 V

Work Functions: (i.e. Fermi Level wrt Vacuum)
Surface Orientation: 001 -> -4.23 V
Surface Orientation: 101 -> -4.52 V
Surface Orientation: 100 -> -4.15 V
Surface Orientation: 212 -> -4.26 V
```

I've chosen these surface terminations to calculate the potential offsets, as they are the most stable surface miller indices (accounting for > 91% of the predicted Wulff shape surface area (see above)).

As is usually the case (from what I can tell from a quick scan of the literature), the work function is indeed surface-dependent, but not massively variable between the most stable surfaces (depending on your reference though, I suppose...). In this case, the work function varies over ~0.4 V.

The fact that the 100 termination gives the highest (least negative) value, suggests that 'thicker' SnO platelets will have higher work functions, compared to the thinner platelets.

Below is the calculated surface-area-normalised values (using the predict Wulff shape):

In [16]:
```
normalized_wulff_areas = {'212': 0.160, '101': 0.111, '100': 0.205, 
'001': 0.437}
total = np.sum(list(normalized_wulff_areas.values()))
for dictionary in [ionisation_potentials, electron_affinities, work
_functions]:
    surface_weighted = 0
    for key, val in normalized_wulff_areas.items():
        surface_weighted += (val/total)*(dictionary[key])
    dictionary["Wulff-shape surface weighted"] = surface_weighted
print("Wulff shape surface-weighted values:")
print(f"Ionisation Potential: (i.e. VBM wrt Vacuum) -> {ionisation_
potentials['Wulff-shape surface weighted']:.2f} V")
print(f"Electron Affinitie: (i.e. CBM wrt Vacuum) -> {electron_affi
nities['Wulff-shape surface weighted']:.2f} V")
print(f"Work Function: (i.e. Fermi Level wrt Vacuum) -> {work_funct
ions['Wulff-shape surface weighted']:.2f} V")
```

```
Wulff shape surface-weighted values:
Ionisation Potential: (i.e. VBM wrt Vacuum) -> -4.47 V
Electron Affinitie: (i.e. CBM wrt Vacuum) -> -3.79 V
Work Function: (i.e. Fermi Level wrt Vacuum) -> -4.25 V
```

Calculated ionisation potential: 4.47 eV
Other (slightly-older theory) calculation(s): 4.4 eV (https://doi.org/10.1021/cm401343a (https://doi.org/10.1021/cm401343a))

Calculated electron affinity: 3.79 eV
Other (slightly-older theory) calculation(s): 3.7 eV (https://doi.org/10.1021/cm401343a (https://doi.org/10.1021/cm401343a))

Calculated work function: 4.25 eV
Experimental work function measurements: 4.3 eV (https://doi.org/10.1063/1.4916664 (https://doi.org/10.1063/1.4916664)) (UPS, SnO Films - i.e. the 001 surface, for which the calculated work function is 4.23 eV), 4.9 eV (https://doi.org/10.1021/cm401343a)(Kelvin (https://doi.org/10.1021/cm401343a)(Kelvin) probe), 5.2 eV (https://iopscience.iop.org/article/10.1088/0957-4484/27/33/335603/meta (https://iopscience.iop.org/article/10.1088/0957-4484/27/33/335603/meta))

Seems to match up pretty damn well with experiment....

Again, these calculations give the ionisation potential, electron affinities and work functions **with respect to vacuum** (i.e. essentially corresponding to measurements in vacuum or air (wouldn't massively affect surface dipoles in this case)), and so solvent effects could still affect these values.

I don't know if any of this is useful / relevant, but hopefully it is! If there's any other particular analysis you think would be interesting / possible, let me know.

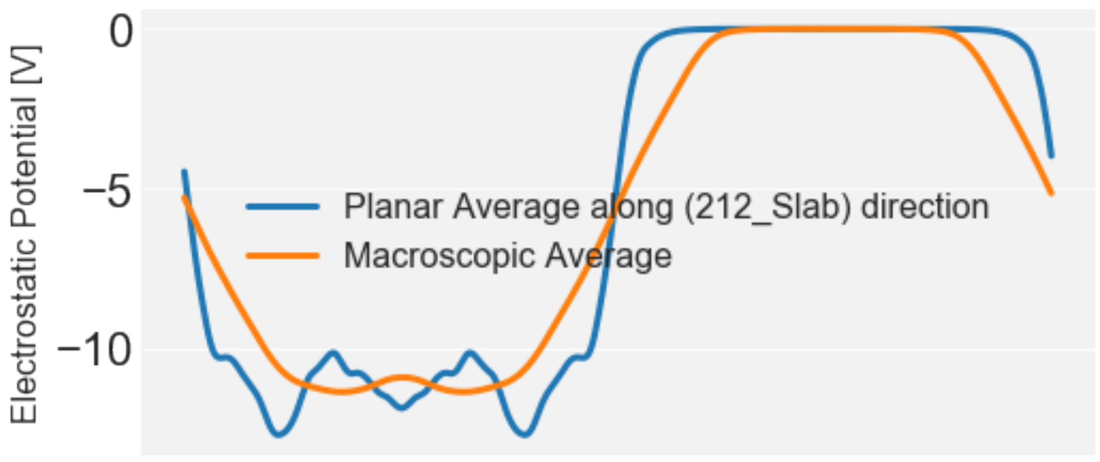
Appendix

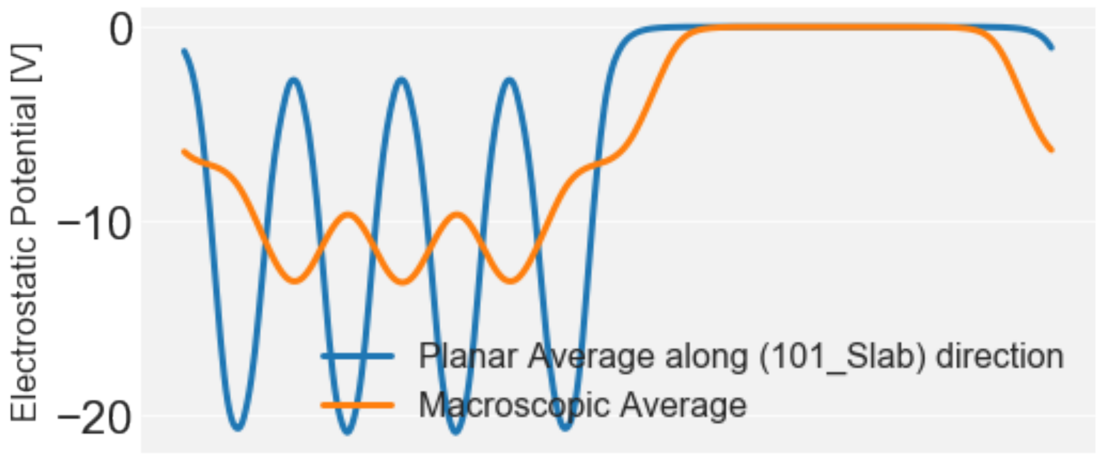
Electrostatic Potential Plots

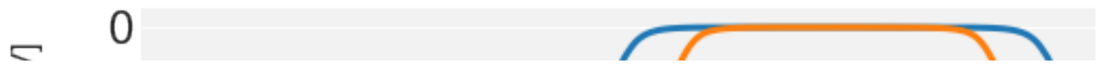
In [52]:
```
planar_data = {}
macro_data = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/"):
    for name in files:
        if "_Slab" in root[-10:]:
            if "LOCPOT" == name:
                input_file = os.path.join(root, name)
                lattice_vector = (4.8)
                output_file = 'whofuckingcares.dat'
                vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_den
sity(
                    input_file, quiet=True)  # execute our now mute
functions
                vector_a, vector_b, vector_c, av, bv, cv = md.matri
x_2_abc(
                    Lattice)
                resolution_x = vector_a/NGX
                resolution_y = vector_b/NGY
                resolution_z = vector_c/NGZ
                grid_pot, electrons = md.density_2_grid(
                    vasp_pot, NGX, NGY, NGZ)
                planar_data[root[-8:]
                            ] = md.planar_average(grid_pot, NGX, NG
Y, NGZ)
                macro_data[root[-8:]] = md.macroscopic_average(
                    planar_data[root[-8:]], lattice_vector, resolut
ion_z)
```

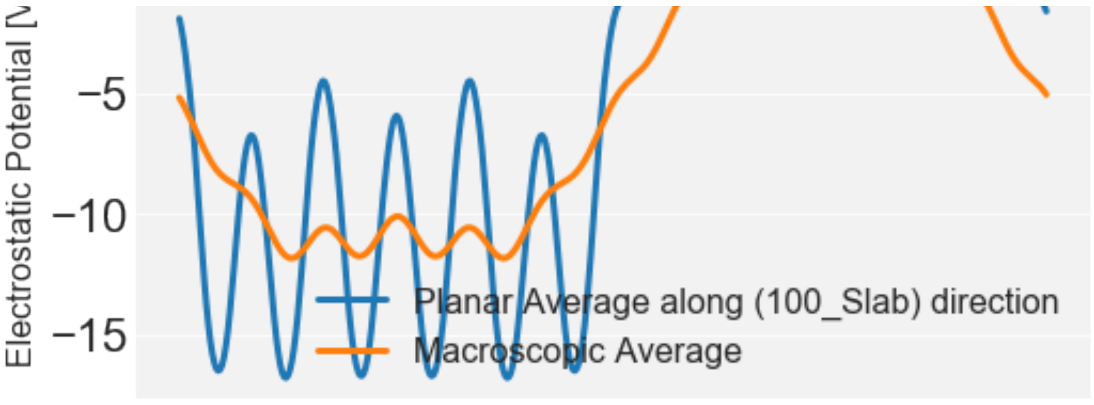
```
Reading header information...
Reading 3D data using Pandas...
Average of the average =  3.684295666904223e-15
Reading header information...
Reading 3D data using Pandas...
Average of the average =  6.158037043254202e-15
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.1419436824715896e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  5.921189464667502e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  2.3021584638627245e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.001526903738046e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -2.590435802371108e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.597029387041749e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  1.5370924487871556e-14
Reading header information...
Reading 3D data using Pandas...
Average of the average =  1.2823875294998287e-13
Reading header information...
Reading 3D data using Pandas...
Average of the average =  -1.8947806286936005e-15
```

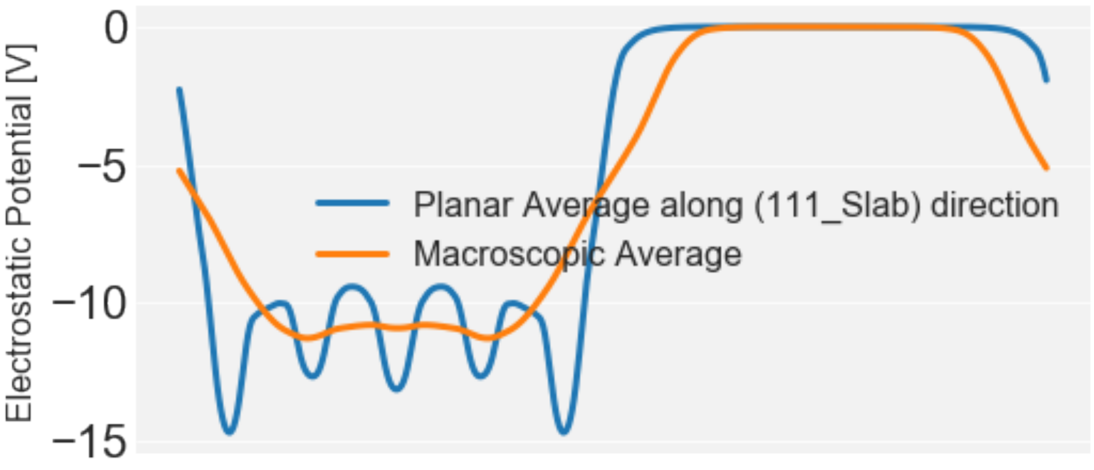
In [53]:
```
%matplotlib inline

fig, ax = plt.subplots(11, 1, figsize=(8, 50))
textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize
mpl.rcParams['ytick.labelsize'] = textsize
plt.rcParams['legend.title_fontsize'] = 22
for i, k in enumerate(planar_data):
    ax[i].plot(planar_data[k]-planar_data[k][350],
               label=f"Planar Average along ({k}) direction", lw=3)
for i, k in enumerate(macro_data):
    ax[i].plot(macro_data[k]-macro_data[k][350],
               label="Macroscopic Average", lw=3)
    ax[i].set_ylabel('Electrostatic Potential [V]', fontsize=16)
    ax[i].get_xaxis().set_visible(False)
    ax[i].grid(True)
    ax[i].legend(fontsize=16)
plt.setp(ax, facecolor=((0.95, 0.95, 0.95)))
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

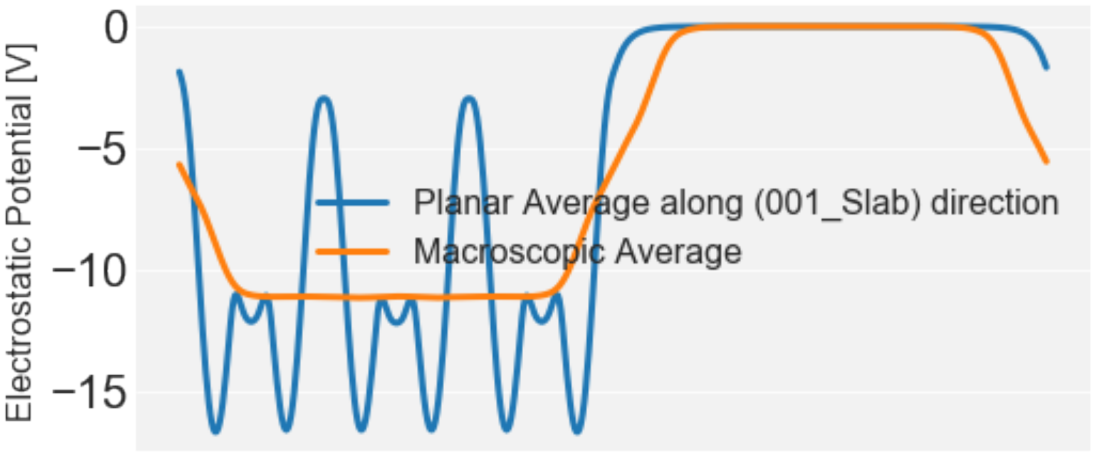


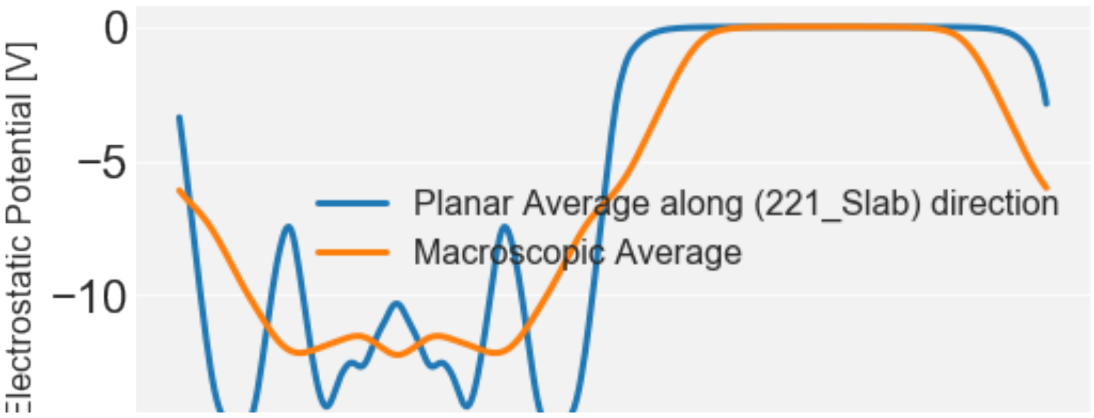




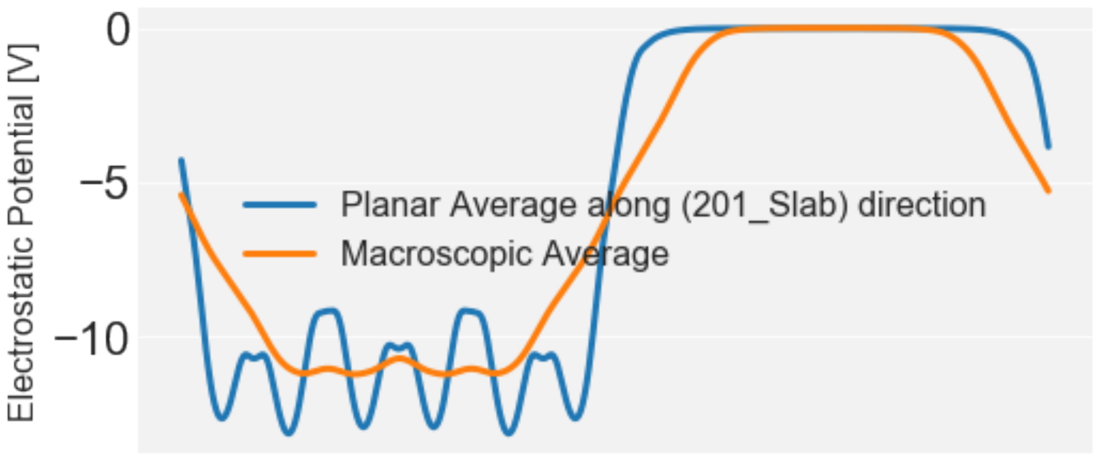

Electrostatic Potential [V
−5
−10
−15
Planar Average along (100_Slab) direction
Macroscopic Average


Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (111_Slab) direction
Macroscopic Average

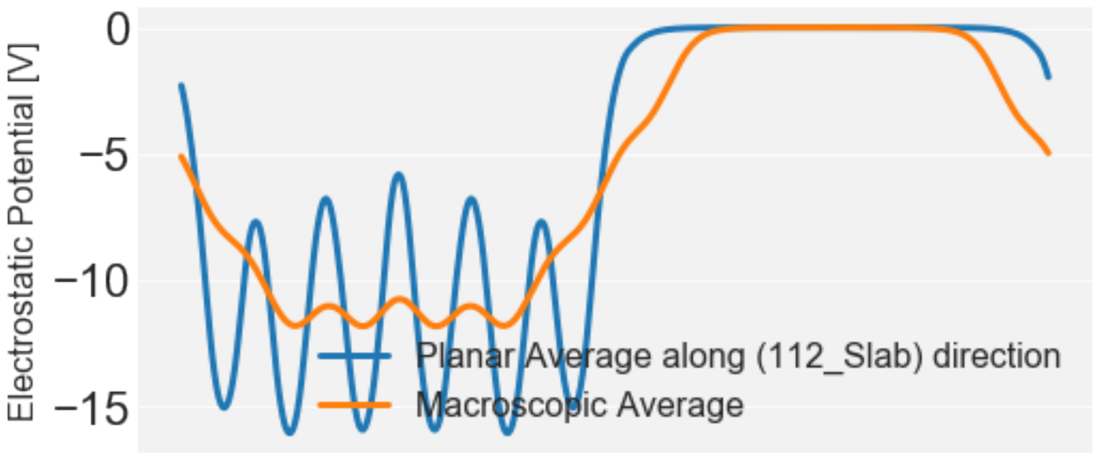

Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (001_Slab) direction
Macroscopic Average


Electrostatic Potential [V]
0
−5
−10
Planar Average along (221_Slab) direction
Macroscopic Average

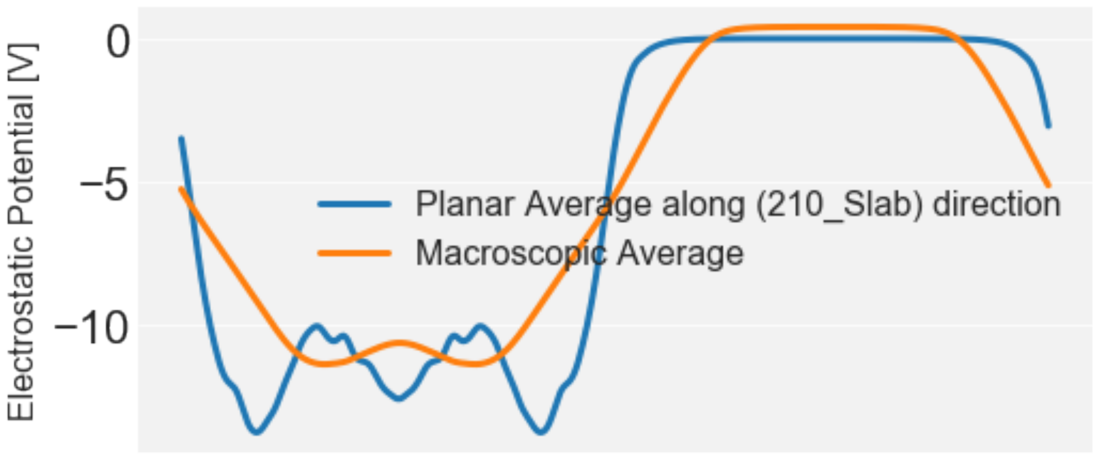
−15



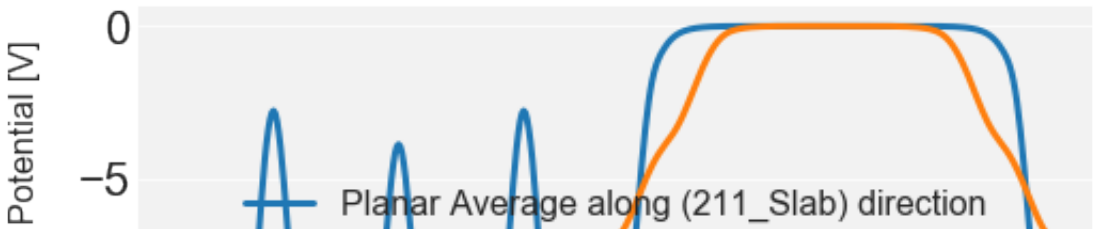
Electrostatic Potential [V]
0
−5
−10
Planar Average along (201_Slab) direction
Macroscopic Average



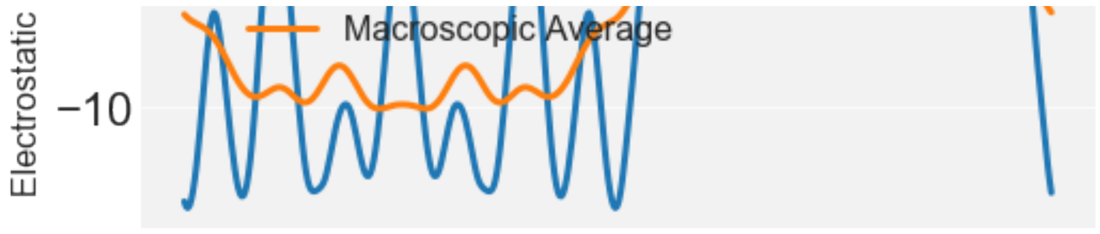
Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (112_Slab) direction
Macroscopic Average

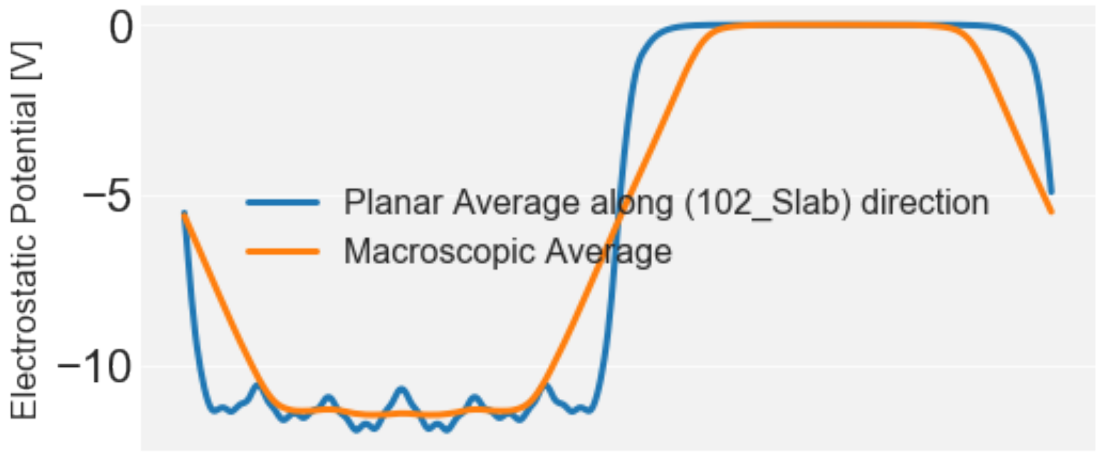


Electrostatic Potential [V]
0
−5
−10
Planar Average along (210_Slab) direction
Macroscopic Average



Potential [V]
0
−5
Planar Average along (211_Slab) direction





Supercell Slab Surface Areas

In [164]:
```python
for i in dipole_free_slabs_vacthic_10:
    print(i.miller_index,
          f"\t -\t Surface Area of Slab: {i.surface_area:.3f}
Angstrom^2")
```

```
(1, 1, 1)       -       Surface Area of Slab: 29.838 Angstrom^2
(2, 2, 1)       -       Surface Area of Slab: 53.984 Angstrom^2
(2, 1, 2)       -       Surface Area of Slab: 50.490 Angstrom^2
(2, 1, 2)       -       Surface Area of Slab: 50.490 Angstrom^2
(2, 1, 1)       -       Surface Area of Slab: 43.615 Angstrom^2
(2, 1, 0)       -       Surface Area of Slab: 41.069 Angstrom^2
(1, 0, 1)       -       Surface Area of Slab: 23.516 Angstrom^2
(2, 0, 1)       -       Surface Area of Slab: 39.560 Angstrom^2
(1, 0, 0)       -       Surface Area of Slab: 18.366 Angstrom^2
(1, 1, 2)       -       Surface Area of Slab: 39.208 Angstrom^2
(1, 0, 2)       -       Surface Area of Slab: 34.641 Angstrom^2
(1, 0, 2)       -       Surface Area of Slab: 34.641 Angstrom^2
(0, 0, 1)       -       Surface Area of Slab: 14.685 Angstrom^2
```

Supercell-size (Slab and Vacuum) Convergence Testing

Convergence Testing (wrt Slab and Vacuum thicknesses) for (001)

Note that convergence within 0.02 J/m^2 is considered sufficiently accurate (see https://www.nature.com/articles/sdata201680 (https://www.nature.com/articles/sdata201680))

In [26]:
```
import os
structure = optB86bvdW_relaxed
# These are distances in Angstroms
dist = [4, 7, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60]
# We iterate through the distances twice, once for vac, once for sl
ab
for vac in dist:
    for thickness in dist:
        slabgen = SlabGenerator(structure, miller_index=(0, 0, 1),
                                min_slab_size=thickness, min_vacuum
_size=vac, lll_reduce=True)
        slabs = slabgen.get_slabs()
        slab = slabs[1]  # <-- put a number in here!
        # print(slab.miller_index) # just to check!
        if not os.path.exists('VASP_Files/optB86b-vdW/001_Slabs/sla
b_{0}_{1}/'.format(thickness, vac)):
            os.makedirs(
                'VASP_Files/optB86b-vdW/001_Slabs/slab_{0}_{1}/'.fo
rmat(thickness, vac))
        slab.to(
            fmt='poscar', filename='VASP_Files/optB86b-vdW/001_Slab
s/slab_{0}_{1}/POSCAR'.format(thickness, vac))
        optB86bvdW_vasp_files(
            optB86bvdW_relaxed, input_dir='VASP_Files/optB86b-vdW/0
01_Slabs/slab_{0}_{1}'.format(thickness, vac))
```

In [43]:
```
#from pymatgen.entries.computed_entries import ComputedStructureEnt
ry
from pymatgen.io.vasp.outputs import Vasprun
bulk_sno_vasprun = Vasprun("./VASP_Files/optB86b-vdW/bulk_rerun/vas
prun.xml")
bulk_sno_entry = bulk_sno_vasprun.get_computed_entry()
```

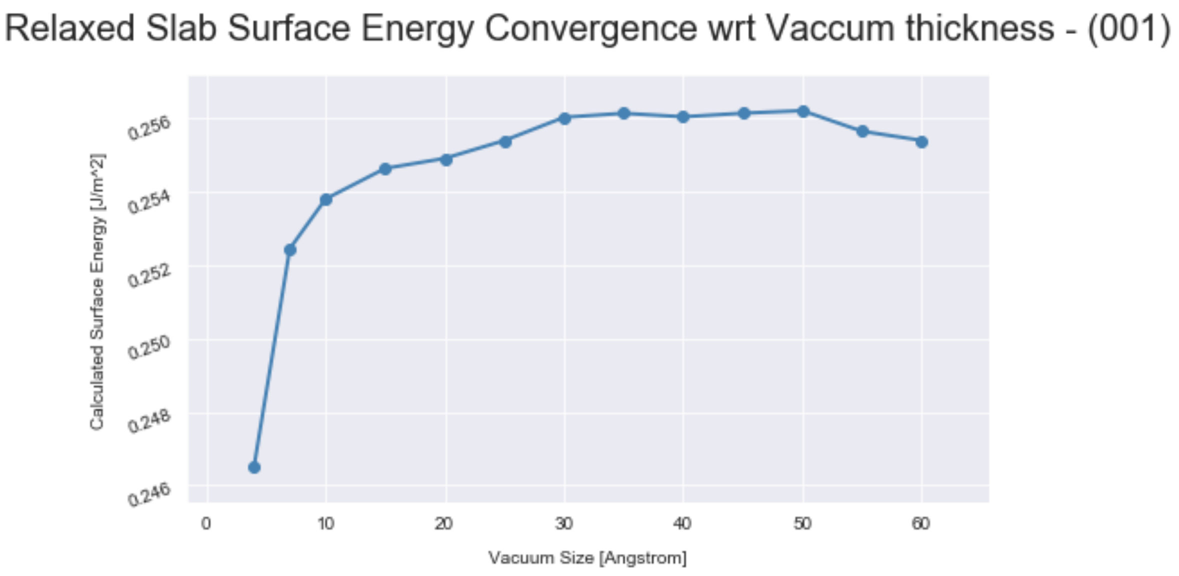
In [17]:
```
import scipy.constants as scpc
```

In [19]:
```
import os
from pymatgen.io.vasp.outputs import Vasprun
from pymatgen.analysis.surface_analysis import SlabEntry
zerozeroone_slabs_vaspruns = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/001_Slab
s/"):
    for name in files:
        if "vasprun" in name:
            #print(os.path.join(root, name))
            zerozeroone_slabs_vaspruns[name] = {'vasprun': Vasprun(
                os.path.join(root, name)), 'thickness': name[5:7],
'vacuum': name[8:10]}
for k, v in zerozeroone_slabs_vaspruns.items():
    v['final_energy'] = v['vasprun'].final_energy
    v['SlabEntry'] = SlabEntry.from_computed_structure_entry(
        v['vasprun'].get_computed_entry(), (0, 0, 1))
    v['SurfaceEnergyJm2'] = v['SlabEntry'].surface_energy(
        bulk_sno_entry)*scpc.electron_volt*10**20  # Convert eV/A^2
to J/m^2
```

In [20]:
```
zerozeroonevac10_thic = []
zerozeroonevac10_energy = []
for k, v in zerozeroone_slabs_vaspruns.items():
    if v['vacuum'] == '10':
        zerozeroonevac10_thic.append(float(v['thickness']))
        zerozeroonevac10_energy.append(v['SurfaceEnergyJm2'])
        zerozeroonevac10 = sorted(
            zip(zerozeroonevac10_thic, zerozeroonevac10_energy), ke
y=lambda t: t[0])
```

In [21]:
```
import numpy as np
import matplotlib.pyplot as plt
import seaborn as sns

%matplotlib inline
sns.set_palette(sns.color_palette('bright'))
sns.set_style('darkgrid')
```

In [31]:
```
f, ax = plt.subplots(1, 1, figsize=(8, 6))
ax.plot(*zip(*zerozeroonevac10), marker="o",
        linewidth=2, linestyle='-', color='steelblue')
ax.grid(True)
ax.set_xlabel("Vacuum Size [Angstrom]", labelpad=10)
ax.set_ylabel("Calculated Surface Energy [J/m^2]", labelpad=10)
ax.set_title("Relaxed Slab Surface Energy Convergence wrt Vaccum th
ickness - (001)",
             fontsize=20, pad=20)  # pad is offset of title from pl
ot
# Adjusting the in-plot margins (i.e. the gap between the final x v
alue and the x limit of the graph)
ax.margins(0.1)
ax.ticklabel_format(useOffset=False)
plt.setp(ax.get_yticklabels(), rotation=20)
f.subplots_adjust(bottom=0.3, top=0.85)  # Adjusting specific margi
ns
```



Ok cool, 10 Angstrom vac, 10 Angstrom slab seems good enough for 001, but other directions might need more (because more broken/dangling bonds)

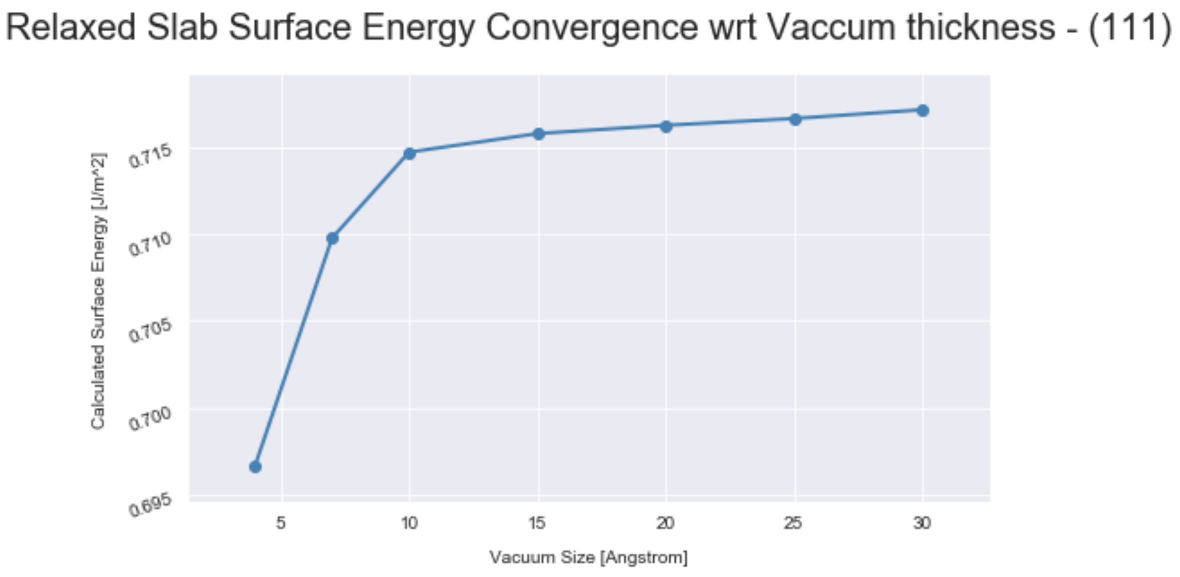
(111) Slab Convergence Test

In [23]:
```
import os
structure = optB86bvdW_relaxed
# These are distances in Angstroms
dist = [4, 7, 10, 15, 20, 25, 30]
# We iterate through the distances twice, once for vac, once for sl
ab
for vac in dist:
    for thickness in dist:
        slabgen = SlabGenerator(structure, miller_index=(1, 1, 1),
                                min_slab_size=thickness, min_vacuum
_size=vac, lll_reduce=True)
        slabs = slabgen.get_slabs()
        slab = slabs[1]  # <-- put a number in here!
        # print(slab.miller_index) # just to check!
        if not os.path.exists('VASP_Files/optB86b-vdW/111_Slabs/sla
b_{0}_{1}/'.format(thickness, vac)):
            os.makedirs(
                'VASP_Files/optB86b-vdW/111_Slabs/slab_{0}_{1}/'.fo
rmat(thickness, vac))
        slab.to(
            fmt='poscar', filename='VASP_Files/optB86b-vdW/111_Slab
s/slab_{0}_{1}/POSCAR'.format(thickness, vac))
        optB86bvdW_vasp_files(
            optB86bvdW_relaxed, input_dir='VASP_Files/optB86b-vdW/1
11_Slabs/slab_{0}_{1}'.format(thickness, vac))
```

In [44]:
```
# import scipy.constants as scpc
import os
from pymatgen.io.vasp.outputs import Vasprun
from pymatgen.analysis.surface_analysis import SlabEntry
oneoneone_slabs_vaspruns = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/111_Slab
s/"):
    for name in files:
        if "vasprun" in name:
            #print(os.path.join(root, name))
            oneoneone_slabs_vaspruns[root[-10:]] = {'vasprun': Vasp
run(
                os.path.join(root, name)), 'thickness': root[-5:-3]
, 'vacuum': root[-2:]}
for k, v in oneoneone_slabs_vaspruns.items():
    v['final_energy'] = v['vasprun'].final_energy
    v['SlabEntry'] = SlabEntry.from_computed_structure_entry(
        v['vasprun'].get_computed_entry(), (1, 1, 1))
    v['SurfaceEnergyJm2'] = v['SlabEntry'].surface_energy(
        bulk_sno_entry)*scpc.electron_volt*10**20  # Convert eV/A^2
to J/m^2
   # v['TestSurfaceEnergy'] = ((v['final_energy']-(7*bulk_sno_entry
.energy))/(2*14.68537370963767))*scpc.electron_volt*10**20 # Conver
t eV/A^2 to J/m^2
```

In [30]:
```
oneoneonethic10_vac = []
oneoneonethic10_energy = []
for k, v in oneoneone_slabs_vaspruns.items():
    if v['thickness'] == '10':
        oneoneonethic10_vac.append(float(v['vacuum']))
        oneoneonethic10_energy.append(v['SurfaceEnergyJm2'])
        oneoneonethic10 = sorted(
            zip(oneoneonethic10_vac, oneoneonethic10_energy), key=l
ambda t: t[0])
```

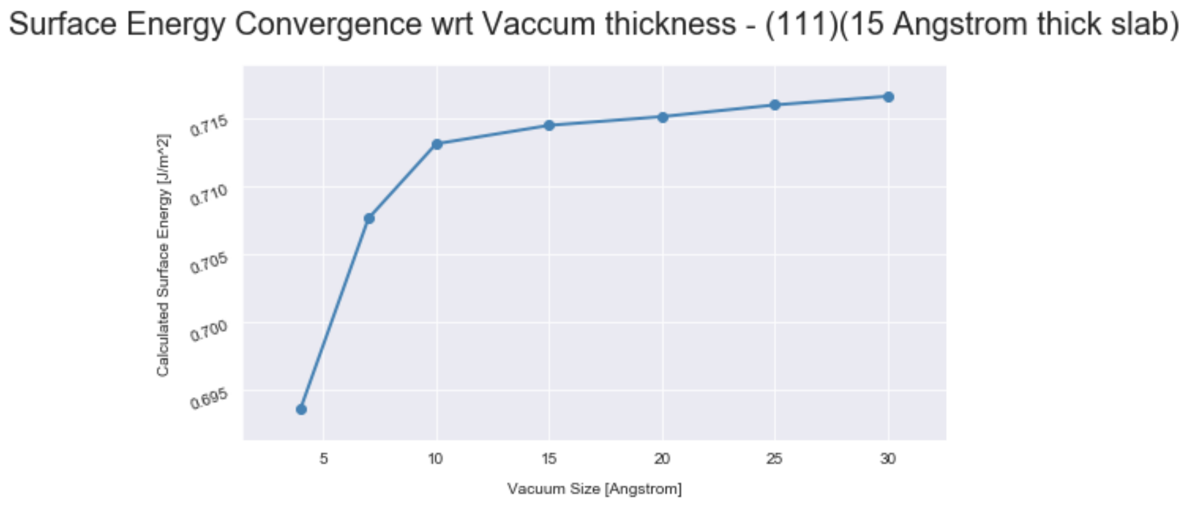
In [32]:
```
f, ax = plt.subplots(1, 1, figsize=(8, 6))
ax.plot(*zip(*oneoneonethic10), marker="o",
        linewidth=2, linestyle='-', color='steelblue')
ax.grid(True)
ax.set_xlabel("Vacuum Size [Angstrom]", labelpad=10)
ax.set_ylabel("Calculated Surface Energy [J/m^2]", labelpad=10)
ax.set_title("Relaxed Slab Surface Energy Convergence wrt Vaccum th
ickness - (111)",
             fontsize=20, pad=20)  # pad is offset of title from pl
ot
# Adjusting the in-plot margins (i.e. the gap between the final x v
alue and the x limit of the graph)
ax.margins(0.1)
ax.ticklabel_format(useOffset=False)
plt.setp(ax.get_yticklabels(), rotation=20)
f.subplots_adjust(bottom=0.3, top=0.85)  # Adjusting specific margi
ns
```



Converged at 10 Angstrom vacuum. Double check with 15 Angstrom thick slabs (so that vacuum convergence doesn't depend on slab thickness, which it shouldn't...), then just stick with 10 Angstrom vacuum and converge wrt slab size.

In [33]:
```
oneoneonethic15_vac = []
oneoneonethic15_energy = []
for k, v in oneoneone_slabs_vaspruns.items():
    if v['thickness'] == '15':
        oneoneonethic15_vac.append(float(v['vacuum']))
        oneoneonethic15_energy.append(v['SurfaceEnergyJm2'])
        oneoneonethic15 = sorted(
            zip(oneoneonethic15_vac, oneoneonethic15_energy), key=l
ambda t: t[0])
```

In [35]:
```
f, ax = plt.subplots(1, 1, figsize=(8, 6))
ax.plot(*zip(*oneoneonethic15), marker="o",
        linewidth=2, linestyle='-', color='steelblue')
ax.grid(True)
ax.set_xlabel("Vacuum Size [Angstrom]", labelpad=10)
ax.set_ylabel("Calculated Surface Energy [J/m^2]", labelpad=10)
ax.set_title("Surface Energy Convergence wrt Vaccum thickness - (11
1)(15 Angstrom thick slab)",
             fontsize=20, pad=20)  # pad is offset of title from pl
ot
# Adjusting the in-plot margins (i.e. the gap between the final x v
alue and the x limit of the graph)
ax.margins(0.1)
ax.ticklabel_format(useOffset=False)
plt.setp(ax.get_yticklabels(), rotation=20)
f.subplots_adjust(bottom=0.3, top=0.85)  # Adjusting specific margi
ns
```

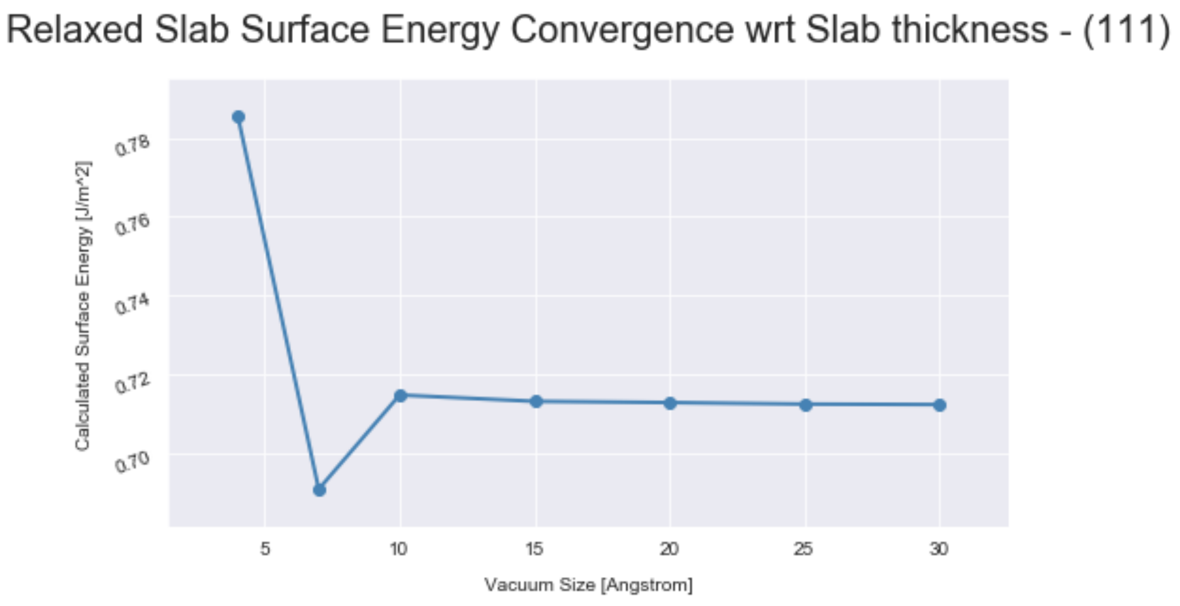


Yep, still converged at 10 Angstrom vac. Let's run convergence test wrt slab thickness, at 10 Angstrom vacuums.

In [45]:
```
# import scipy.constants as scpc
import os
from pymatgen.io.vasp.outputs import Vasprun
from pymatgen.analysis.surface_analysis import SlabEntry
oneoneone_slabs_vaspruns = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/111_Slab
s/"):
    for name in files:
        if "vasprun" in name:
            #print(os.path.join(root, name))
            oneoneone_slabs_vaspruns[root[-10:]] = {'vasprun': Vasp
run(
                os.path.join(root, name)), 'thickness': root[-5:-3]
, 'vacuum': root[-2:]}
for k, v in oneoneone_slabs_vaspruns.items():
    v['final_energy'] = v['vasprun'].final_energy
    v['SlabEntry'] = SlabEntry.from_computed_structure_entry(
        v['vasprun'].get_computed_entry(), (1, 1, 1))
    v['SurfaceEnergyJm2'] = v['SlabEntry'].surface_energy(
        bulk_sno_entry)*scpc.electron_volt*10**20  # Convert eV/A^2
to J/m^2
```

In [37]:
```
oneoneonevac10_thic = []
oneoneonevac10_energy = []
for k, v in oneoneone_slabs_vaspruns.items():
    if v['vacuum'] == '10':
        oneoneonevac10_thic.append(float(v['thickness']))
        oneoneonevac10_energy.append(v['SurfaceEnergyJm2'])
        oneoneonevac10 = sorted(
            zip(oneoneonevac10_thic, oneoneonevac10_energy), key=la
mbda t: t[0])
```

In [38]:
```
f, ax = plt.subplots(1, 1, figsize=(8, 6))
ax.plot(*zip(*oneoneonevac10), marker="o",
        linewidth=2, linestyle='-', color='steelblue')
ax.grid(True)
ax.set_xlabel("Vacuum Size [Angstrom]", labelpad=10)
ax.set_ylabel("Calculated Surface Energy [J/m^2]", labelpad=10)
ax.set_title("Relaxed Slab Surface Energy Convergence wrt Slab thic
kness - (111)",
             fontsize=20, pad=20)  # pad is offset of title from pl
ot
# Adjusting the in-plot margins (i.e. the gap between the final x v
alue and the x limit of the graph)
ax.margins(0.1)
ax.ticklabel_format(useOffset=False)
plt.setp(ax.get_yticklabels(), rotation=20)
f.subplots_adjust(bottom=0.3, top=0.85)  # Adjusting specific margi
ns
```



Ayo, yeah slab and vacuum thicknesses both converged at 10 Angstrom respectively.

Structural Relaxation

(Functional, calculation parameters, results)

In all cases; α = 90, β = 90, γ = 90

PBEsol: - `ENCUT = 850` , ***k***-mesh = $7 \times 7 \times 5$

a,*b* = 3.810, *c* = 4.754

PBEsol + D3: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$

a,*b* = 3.768, *c* = 4.565

PBEsol + SOC + D3: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$

a,*b* = 3.762, *c* = 4.523

PBE + D3: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$

a,*b* = 3.824, *c* = 4.736

PBE + SOC + D3: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$

a,*b* = 3.819, *c* = 4.683

SCAN+rVV10: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$ (Meta-GGA)

a,*b* = 3.772, *c* = 4.644

SOC not possible with SCAN_rVV10.

SCAN: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$ (Meta-GGA)

a,*b* = 3.792, *c* = 4.741

SCAN+SOC: - `ENCUT = 850` , ***k***-mesh = $6 \times 6 \times 4$ (Meta-GGA) *a*,*b* = 3.793, *c* = 4.773

Ground-State Energy Convergence Tests

`PSMAXN` warning encountered for `ENCUT = 900` and above.
Well-converged (to within 1 meV/atom) at `ENCUT = 700` and ***k***-mesh of $6 \times 6 \times 4$ for vanilla GGA.

```
Directory: Total Energy/eV: (per atom): Energy difference meV/atom:
e1000 -24.16974220 -6.0424355
e300 -24.42298528 -6.1057463 63.3108000
e350 -24.22912647 -6.0572816 -48.4647000
e400 -24.19024086 -6.0475602 -9.7214000
e450 -24.16643286 -6.0416082 -5.9520000
e500 -24.15956129 -6.0398903 -1.7179000
e550 -24.16074806 -6.0401870 .2967000
e600 -24.16415629 -6.0410390 .8520000
e650 -24.16679234 -6.0416980 .6590000
e700 -24.16872708 -6.0421817 .4837000
e750 -24.16942997 -6.0423574 .1757000
e800 -24.17004842 -6.0425121 .1547000
e850 -24.16990605 -6.0424765 -.0356000
e900 -24.16974924 -6.0424373 -.0392000
e950 -24.16974061 -6.0424351 -.0022000
```

```
Directory: Total Energy/eV: (per atom): Energy difference meV/atom:
k10107 -24.15958413 -6.0398960
k10108 -24.15957873 -6.0398946 -.0014000
k11118 -24.15957876 -6.0398946 0
k11119 -24.15959391 -6.0398984 .0038000
k121210 -24.15958997 -6.0398974 -.0010000
k12129 -24.15959264 -6.0398981 .0007000
k131310 -24.15958341 -6.0398958 -.0023000
k131311 -24.15959360 -6.0398984 .0026000
k141411 -24.15958531 -6.0398963 -.0021000
k151511 -24.15958344 -6.0398958 -.0005000
k151512 -24.15958330 -6.0398958 0
k222 -24.23903425 -6.0597585 19.8627000
k332 -24.15674376 -6.0391859 -20.5726000
k333 -24.16719047 -6.0417976 2.6117000
k443 -24.15230648 -6.0380766 -3.7210000
k444 -24.15165377 -6.0379134 -.1632000
k554 -24.15880731 -6.0397018 1.7884000
k664 -24.15956129 -6.0398903 .1885000
k665 -24.15961412 -6.0399035 .0132000
k775 -24.15965218 -6.0399130 .0095000
k776 -24.15962258 -6.0399056 -.0074000
k886 -24.15955116 -6.0398877 -.0179000
k887 -24.15957659 -6.0398941 .0064000
k997 -24.15956960 -6.0398924 -.0017000
```

```
In [ ]:
```