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), 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/10.1103/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)).

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 [1]:
```
from pymatgen.core.surface import SlabGenerator, generate_all_slabs
, Structure, Lattice
import pymatgen.symmetry.analyzer as pmgsyman
```

In [2]:
```
optB86bvdW_relaxed = Structure.from_file("VASP_Files/optB86b-vdW/CO
NTCAR")
optB86bvdW_relaxed.add_oxidation_state_by_guess()
```

Relaxed (predicted) structural parameters:

In [3]:
```
optB86bvdW_relaxed
```

Out[3]:
```
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 [4]:
```
spganalyse_opt = pmgsyman.SpacegroupAnalyzer(optB86bvdW_relaxed)
```

In [13]:
```
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 [15]:
```
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 [136]:
```
#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 [137]:
```
import scipy.constants as scpc
import os
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 [138]:
```
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 [139]:
```
from pymatgen.analysis.wulff import WulffShape
```

In [140]:
```
sno_miller_indices = []
sno_surface_energies_jm2 = []
for k,v in dipolefree_slabs_vaspruns.items():
    if v['miller index'] in [(0,0,1)]:
        c_energy = v['SurfaceEnergyJm2'] # Bug in the code, can't u
se 001 miller index, need to
        # specify as 0.0000000000001, 0, 1
    else:
        sno_miller_indices.append(v['miller index']) # Might need t
o reformat this
        sno_surface_energies_jm2.append(v['SurfaceEnergyJm2'])
sno_miller_indices.append((0.00000000001, 0, 1)) # Bug in the code,
can't use 001 miller index,
# need to specify as 0.0000000000001, 0, 1
sno_surface_energies_jm2.append(c_energy)
wulff_sno = WulffShape(optB86bvdW_relaxed.lattice,sno_miller_indice
s,sno_surface_energies_jm2)
```

In [141]:
```
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 [66]:
```
print("Shape factor: %.3f, Anisotropy: \
%.3f, Weighted surface energy: %.3f J/m^2" %(wulff_sno.shape_factor
,
                                             wulff_sno.anisotropy,
                                             wulff_sno.weighted_surface_e
nergy))
# 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
```

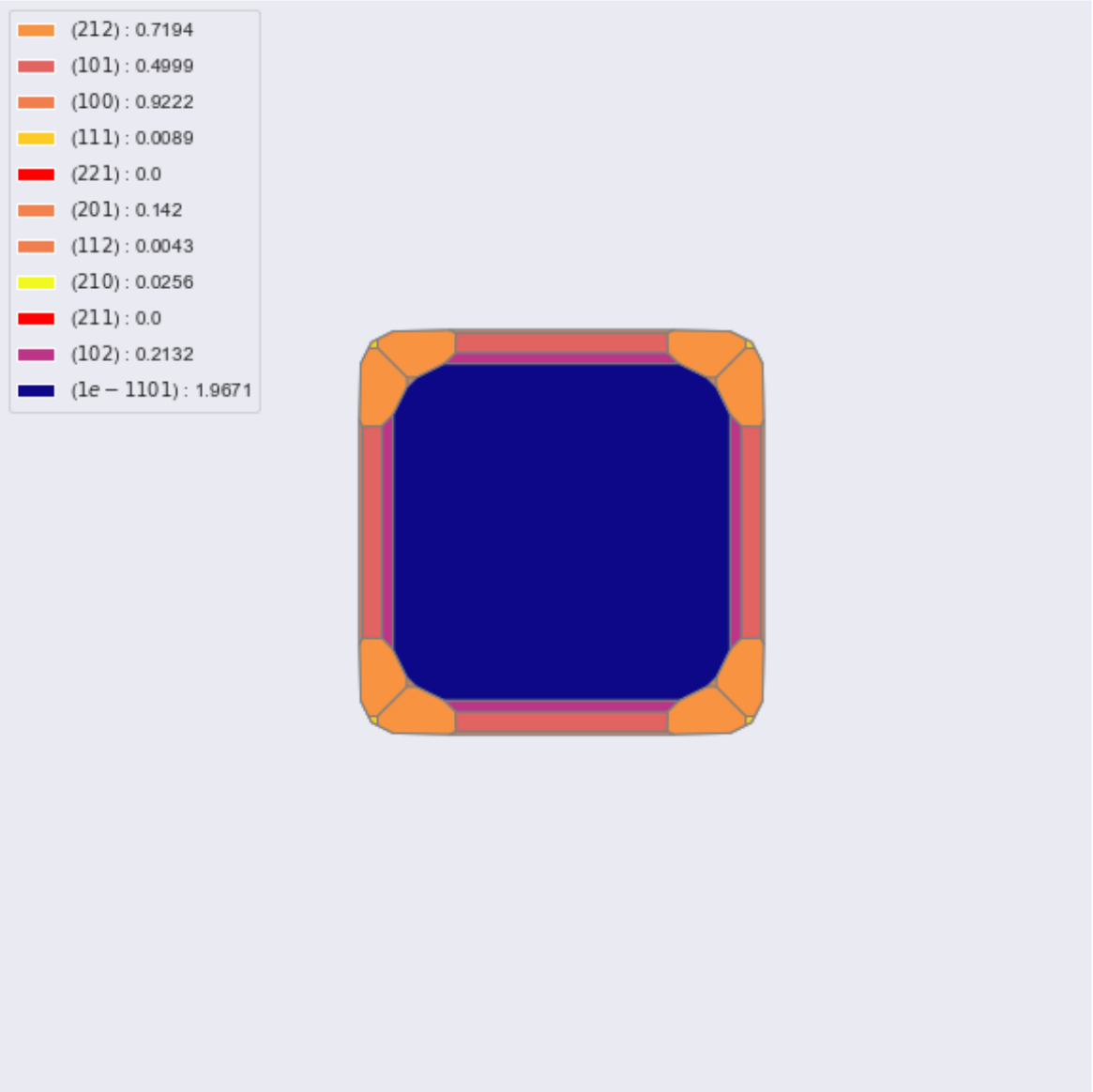
```
Shape factor: 5.853, Anisotropy: 0.391, Weighted surface energy: 0
.450 J/m^2
```

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 [151]:
```
%load_ext autoreload
%autoreload 2
%matplotlib widget
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
```



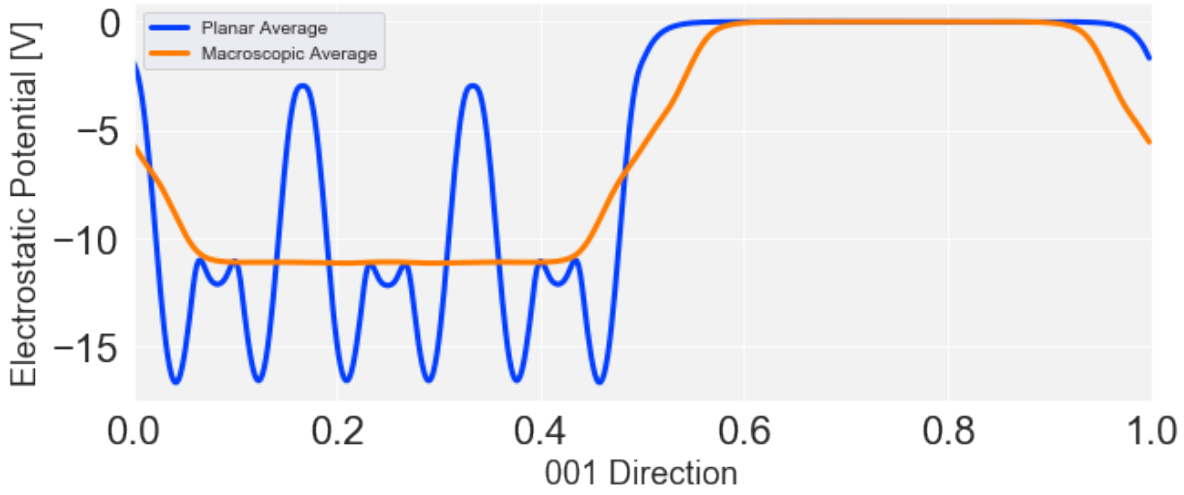
See images and videos for different viewpoints on Wulff Shape. Looks similar to the platelets in the Ethylene Glycol solvent. Suggests that solvents (like H_2O and EtOH) have strong kinetic effects, further stabilising the 001 face relative to other surfaces (-> making thinnner platelets).

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 [67]:
```
import macrodensity as md
import io
import sys
import matplotlib.pyplot as plt; import matplotlib as mpl
```

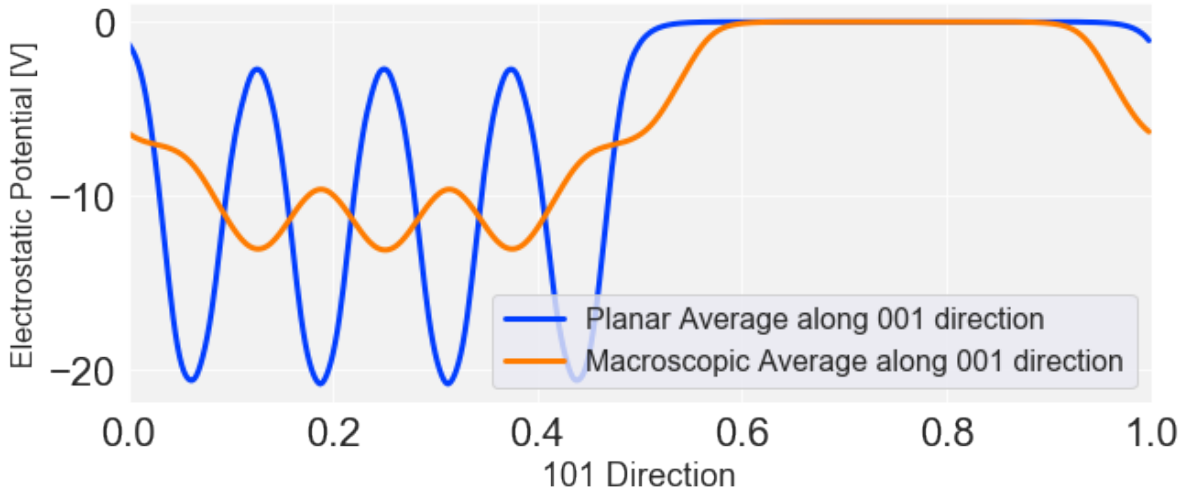
In [82]:
```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/001_Slab/LOCPOT'
lattice_vector = (4.8); output_file = 'whofuckingcares.dat'
# create a text trap and redirect stdout (I've seen Macrodensity's
big BOOM enough fucking times...)
text_trap = io.StringIO(); old_stdout = sys.stdout; sys.stdout = te
xt_trap
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(input_file)
# 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; resolutio
n_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot,NGX,NGY,NGZ)
sys.stdout = old_stdout # now restore stdout function
planar001 = md.planar_average(grid_pot,NGX,NGY,NGZ); macro  = md.ma
croscopic_average(planar001,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.lab
elsize'] = textsize; plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0,1,1.0/len(planar001)), planar001-planar001[400]
,label="Planar Average",lw=3)
ax.plot(np.arange(0,1,1.0/len(planar001)), macro-macro[400],label="
Macroscopic Average",lw=3);
plt.setp(ax, xlim=(0,1), facecolor=((0.95,0.95,0.95))); ax.grid(Tru
e); ax.legend()
ax.set_ylabel('Electrostatic Potential [V]', fontsize = 18)
ax.set_xlabel('001 Direction', fontsize = 18)
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

```
Average of the average =  2.3021584638627245e-13
```



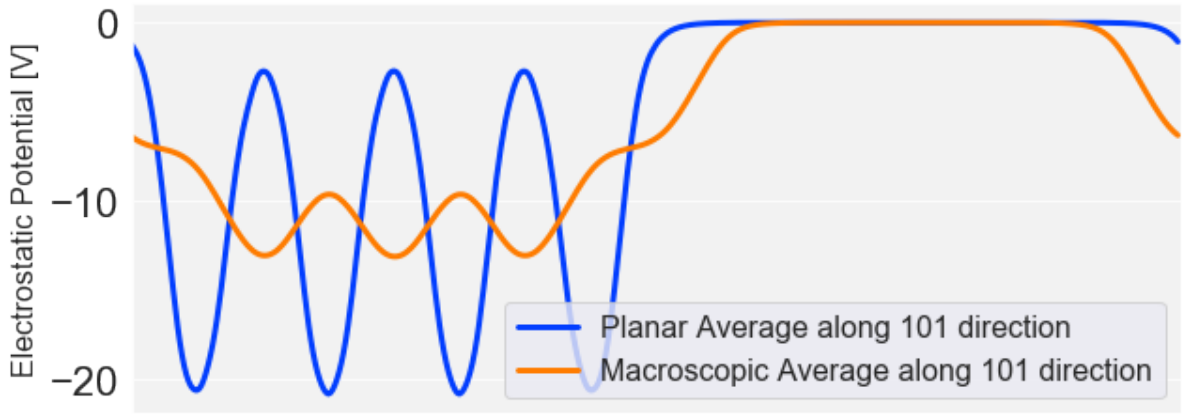
In [102]:
```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/101_Slab/LOCPOT'
lattice_vector = (4.8); output_file = 'whofuckingcares.dat'
# create a text trap and redirect stdout (I've seen Macrodensity's
big BOOM enough fucking times...)
text_trap = io.StringIO(); old_stdout = sys.stdout; sys.stdout = te
xt_trap
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(input_file)
# 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; resolutio
n_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot,NGX,NGY,NGZ)
sys.stdout = old_stdout # now restore stdout function
planar001 = md.planar_average(grid_pot,NGX,NGY,NGZ); macro  = md.ma
croscopic_average(planar001,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.lab
elsize'] = textsize; plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0,1,1.0/len(planar001)), planar001-planar001[400]
,label="Planar Average along 001 direction",lw=3)
ax.plot(np.arange(0,1,1.0/len(planar001)), macro-macro[400],label="
Macroscopic Average along 001 direction",lw=3);
plt.setp(ax, xlim=(0,1), facecolor=((0.95,0.95,0.95))); ax.grid(Tru
e); ax.legend(fontsize = 16)
ax.set_ylabel('Electrostatic Potential [V]', fontsize = 16)
ax.set_xlabel('101 Direction', fontsize = 18)
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

```
Average of the average =  6.158037043254202e-15
```



In [101]:
```
%matplotlib inline
input_file = 'VASP_Files/optB86b-vdW/101_Slab/LOCPOT'
lattice_vector = (4.8); output_file = 'whofuckingcares.dat'
# create a text trap and redirect stdout (I've seen Macrodensity's
big BOOM enough fucking times...)
text_trap = io.StringIO(); old_stdout = sys.stdout; sys.stdout = te
xt_trap
vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(input_file)
# 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; resolutio
n_z = vector_c/NGZ
grid_pot, electrons = md.density_2_grid(vasp_pot,NGX,NGY,NGZ)
sys.stdout = old_stdout # now restore stdout function
planar001 = md.planar_average(grid_pot,NGX,NGY,NGZ); macro  = md.ma
croscopic_average(planar001,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.lab
elsize'] = textsize; plt.rcParams['legend.title_fontsize'] = 22
ax.plot(np.arange(0,1,1.0/len(planar001)), planar001-planar001[400]
,label="Planar Average along 101 direction",lw=3)
ax.plot(np.arange(0,1,1.0/len(planar001)), macro-macro[400],label="
Macroscopic Average along 101 direction",lw=3);
plt.setp(ax, xlim=(0,1), facecolor=((0.95,0.95,0.95))); ax.grid(Tru
e); ax.legend(fontsize = 16)
ax.set_ylabel('Electrostatic Potential [V]', fontsize = 16)
ax.set_xlabel('101 Direction', fontsize = 18)
ax.get_xaxis().set_visible(False)
plt.show()
#print(f"Using plateaus in the centre of each slab: Offset (Bi rela
tive to Sb) = {macro[91]-macro[270]:.4f} V")
```

```
Average of the average =  6.158037043254202e-15
```



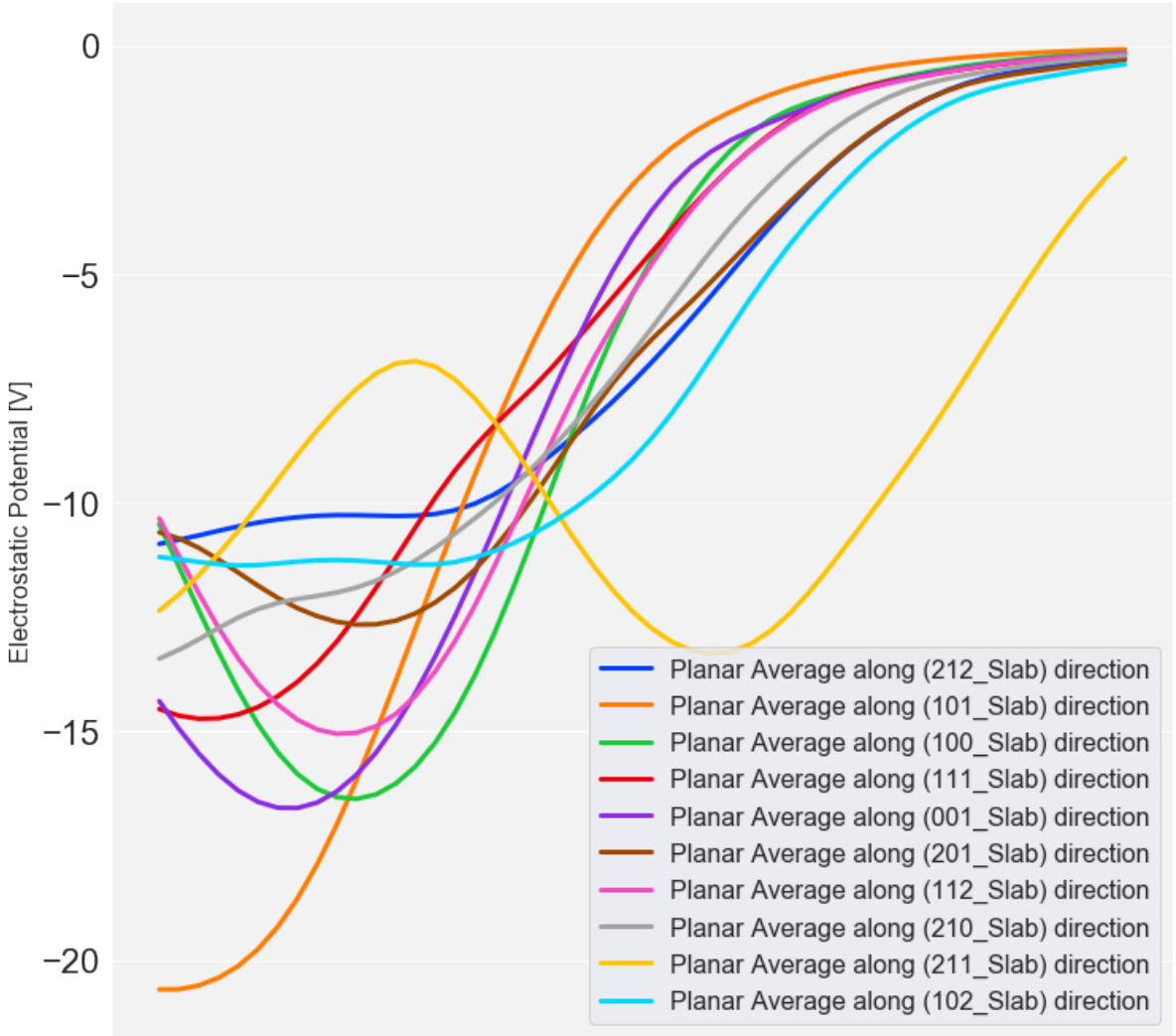
See Appendix: Local Potential Plots for other surfaces, if of interest.

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

In [156]:
```
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" in name:
                if "221" in root:
                    continue
                input_file = os.path.join(root, name)
                lattice_vector = (4.8); output_file = 'whofuckingca
res.dat'
                # create a text trap and redirect stdout (I've seen
Macrodensity's big BOOM enough fucking times...)
                text_trap = io.StringIO(); old_stdout = sys.stdout;
sys.stdout = text_trap
                vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_den
sity(input_file) # execute our now mute functions
                vector_a,vector_b,vector_c,av,bv,cv = md.matrix_2_a
bc(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,NG
X,NGY,NGZ)
                sys.stdout = old_stdout # now restore stdout functi
on
                planar_data[root[-8:]] = md.planar_average(grid_pot
,NGX,NGY,NGZ)
                macro_data[root[-8:]]  = md.macroscopic_average(pla
nar_data[root[-8:]],lattice_vector,resolution_z)
```

```
Average of the average =  3.684295666904223e-15
Average of the average =  6.158037043254202e-15
Average of the average =  -1.1419436824715896e-14
Average of the average =  5.921189464667502e-14
Average of the average =  2.3021584638627245e-13
Average of the average =  -2.590435802371108e-13
Average of the average =  -1.597029387041749e-14
Average of the average =  1.5370924487871556e-14
Average of the average =  1.2823875294998287e-13
Average of the average =  -1.8947806286936005e-15
```

In [157]:
```
%matplotlib inline
fig, ax = plt.subplots(1, 1, figsize=(12,12)); textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize; mpl.rcParams['ytick.lab
elsize'] = 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],l
abel=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 = 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")
```



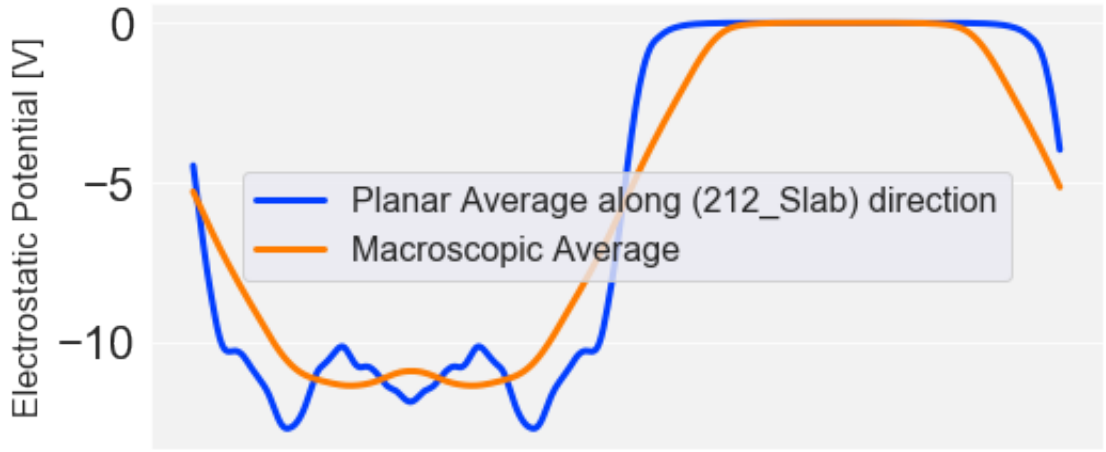
Appendix

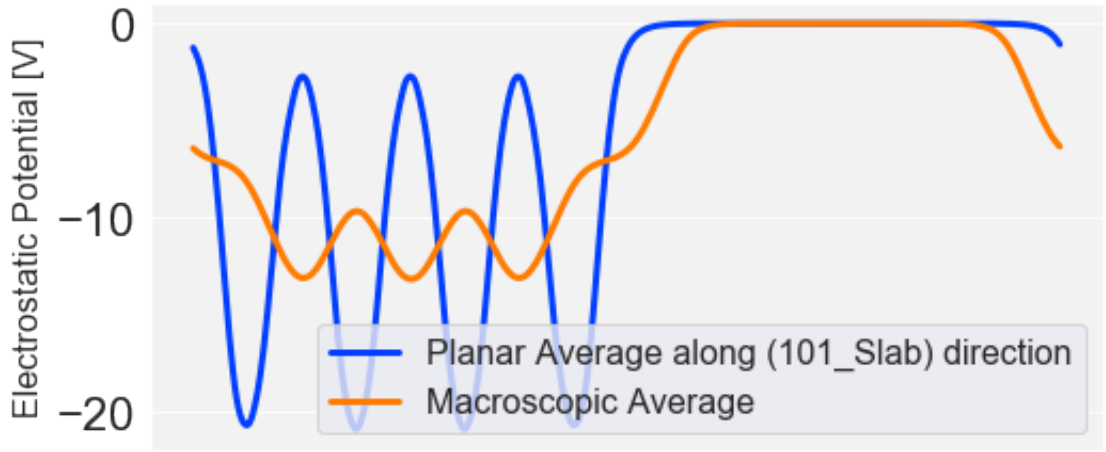
Electrostatic Potential Plots

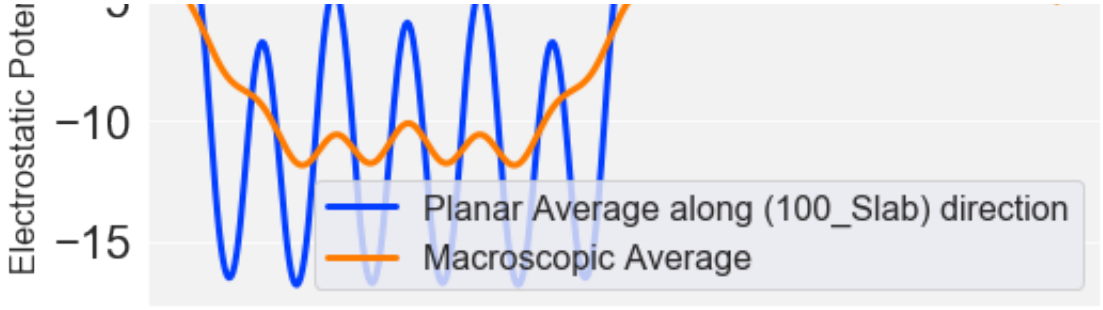
In [88]:
```
planar_data = {}; macro_data = {}
for root, dirs, files in os.walk("./VASP_Files/optB86b-vdW/"):
    for name in files:
        if "_Slab" in root[-10:]:
            if "LOCPOT" in name:
                input_file = os.path.join(root, name)
                lattice_vector = (4.8); output_file = 'whofuckingcares.dat'
                # create a text trap and redirect stdout (I've seen Macrodensity's big BOOM enough fucking times...)
                text_trap = io.StringIO(); old_stdout = sys.stdout; sys.stdout = text_trap
                vasp_pot, NGX, NGY, NGZ, Lattice = md.read_vasp_density(input_file) # 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)
                sys.stdout = old_stdout # now restore stdout function
                planar_data[root[-8:]] = md.planar_average(grid_pot,NGX,NGY,NGZ)
                macro_data[root[-8:]]  = md.macroscopic_average(planar_data[root[-8:]],lattice_vector,resolution_z)
```

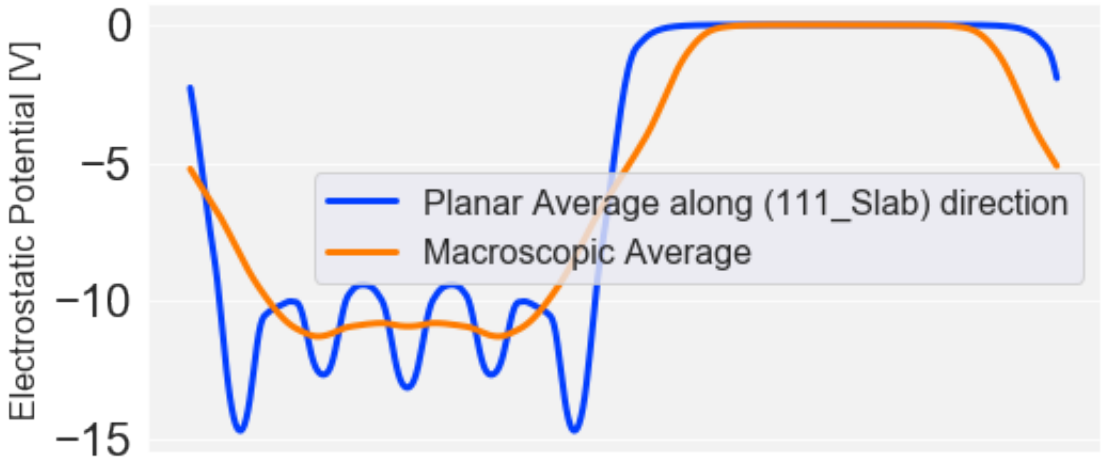
```
Average of the average =  3.684295666904223e-15
Average of the average =  6.158037043254202e-15
Average of the average =  -1.1419436824715896e-14
Average of the average =  5.921189464667502e-14
Average of the average =  2.3021584638627245e-13
Average of the average =  -1.001526903738046e-14
Average of the average =  -2.590435802371108e-13
Average of the average =  -1.597029387041749e-14
Average of the average =  1.5370924487871556e-14
Average of the average =  -1.8947806286936005e-15
```

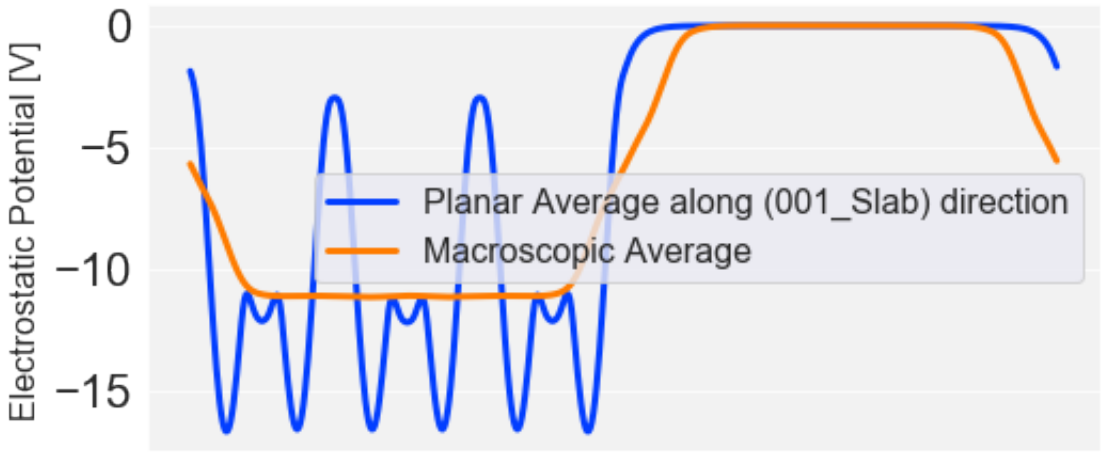
In [155]:
```
%matplotlib inline

fig, ax = plt.subplots(11, 1, figsize=(8,50)); textsize = 22
mpl.rcParams['xtick.labelsize'] = textsize; mpl.rcParams['ytick.lab
elsize'] = 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 Av
erage 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")
```

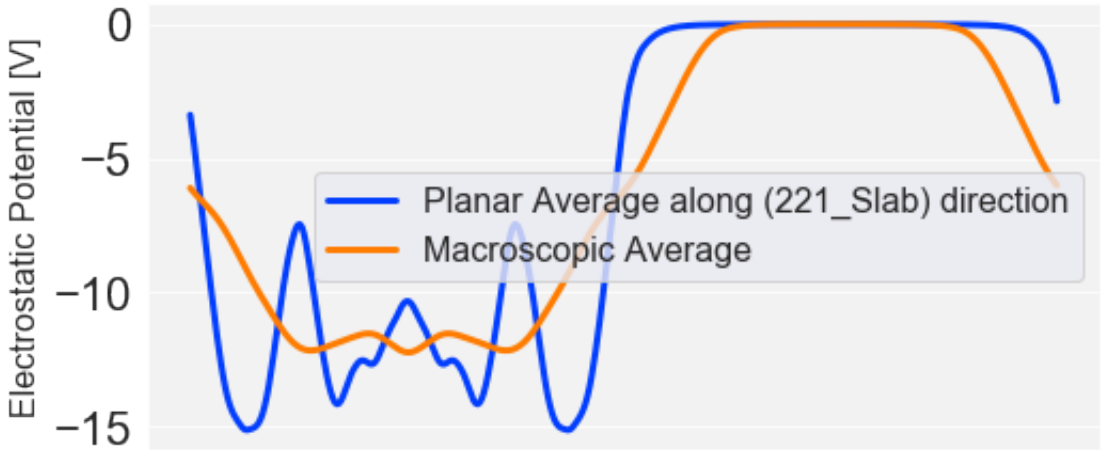


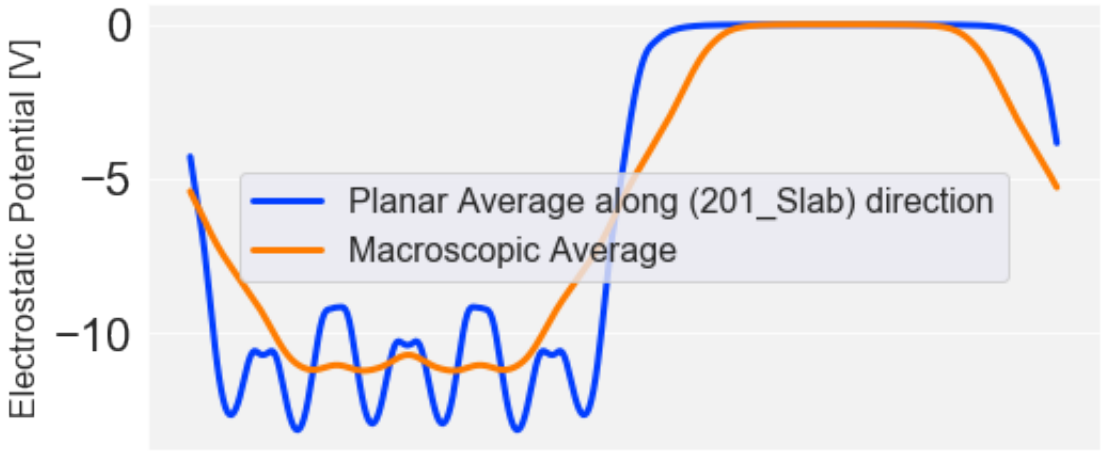


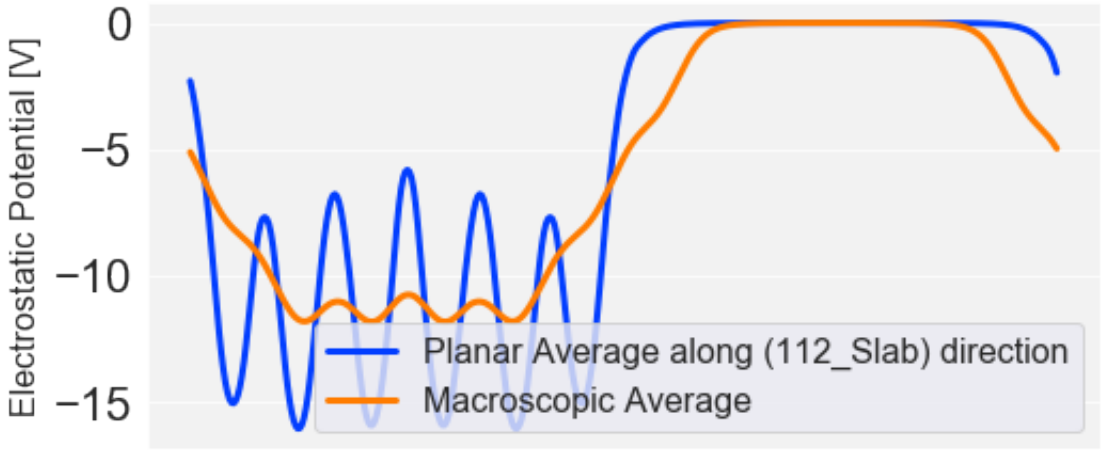

Electrostatic Potential
−10
−15
Planar Average along (100_Slab) direction
Macroscopic Average

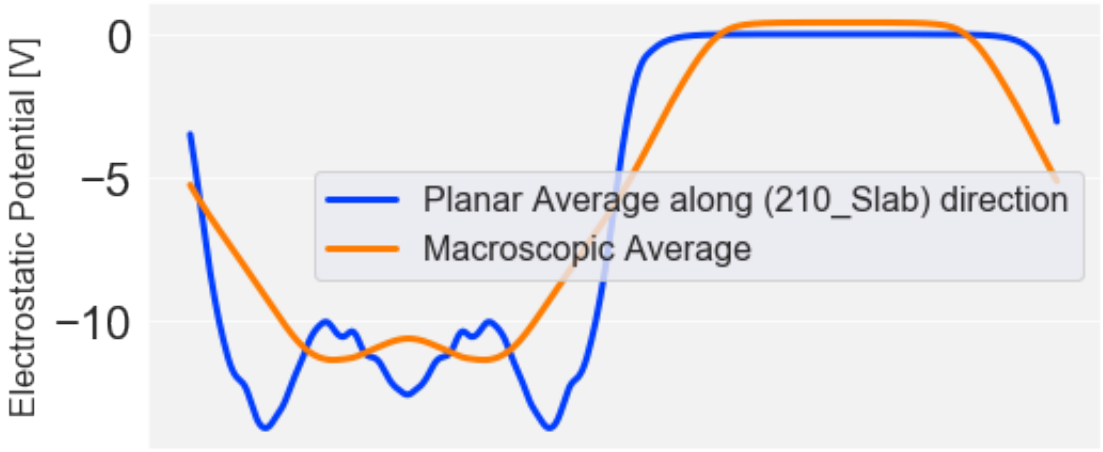

Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (111_Slab) direction
Macroscopic Average

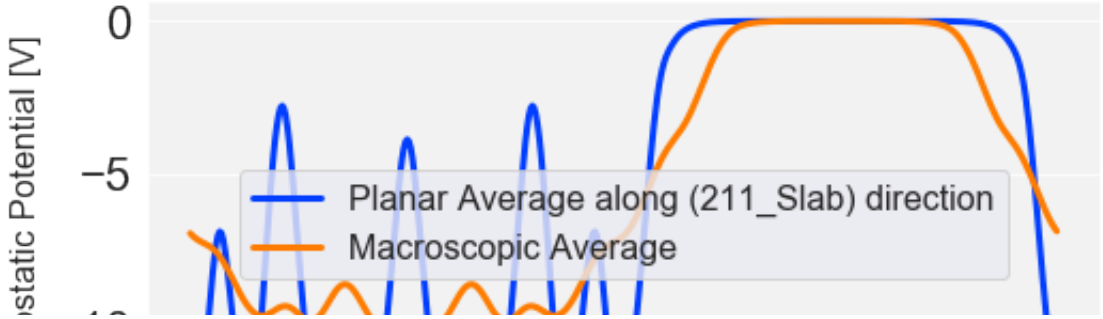

Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (001_Slab) direction
Macroscopic Average

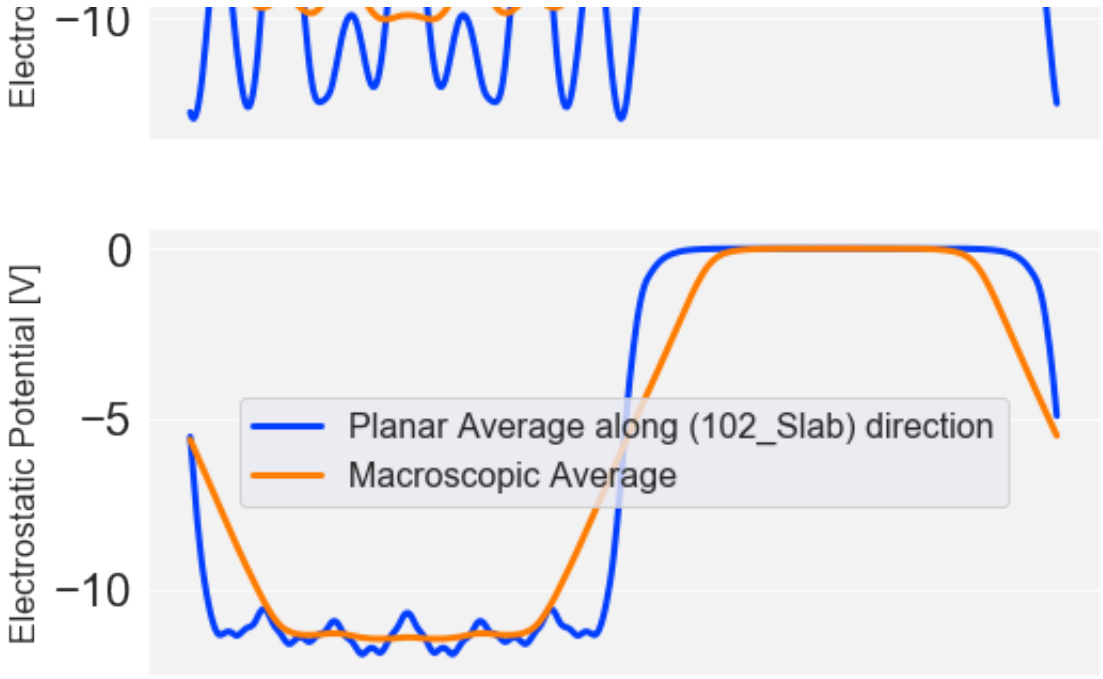

Electrostatic Potential [V]
0
−5
−10
−15
Planar Average along (221_Slab) direction
Macroscopic Average


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


0
−5
Planar Average along (211_Slab) direction
Macroscopic Average



Supercell Slab Surface Areas

In [164]:
```
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}/'.format(thickness,vac))
        slab.to(fmt='poscar', filename='VASP_Files/optB86b-vdW/001_
Slabs/slab_{0}_{1}/POSCAR'.format(thickness,vac))
        optB86bvdW_vasp_files(optB86bvdW_relaxed, input_dir='VASP_F
iles/optB86b-vdW/001_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()
```

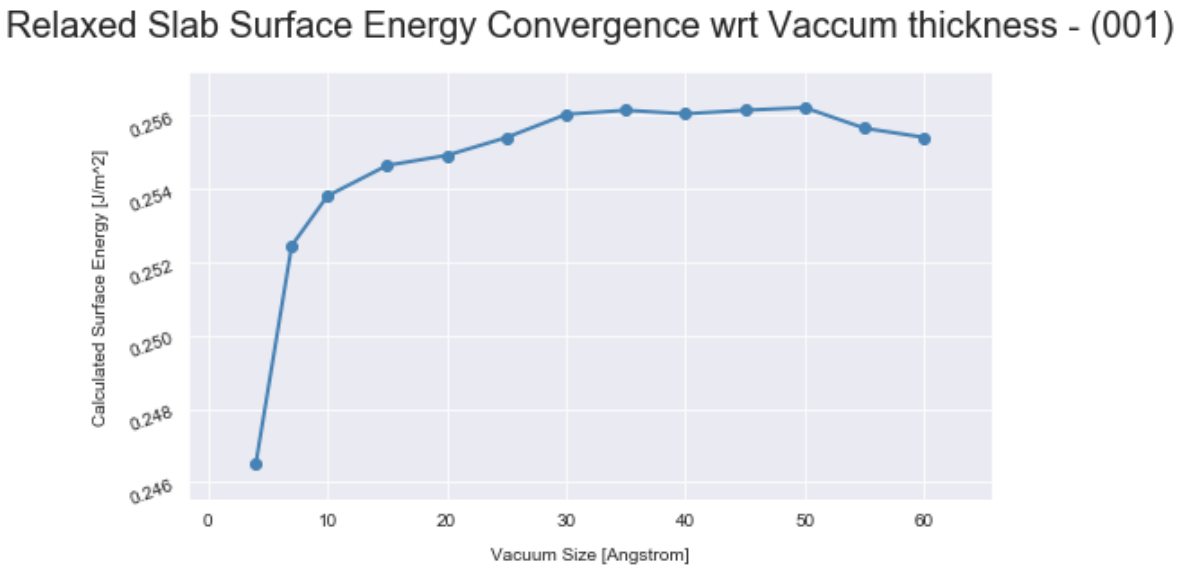
In [17]:
```
import scipy.constants as scpc
```

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_Slabs/"):
    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), key = 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 p
lot
# 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)

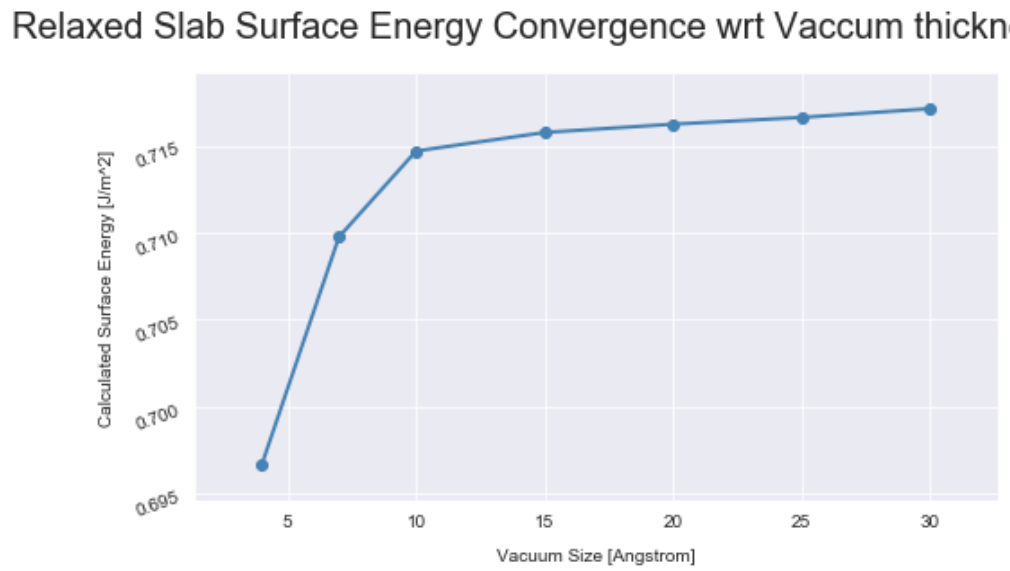
(111) Slab Convergence Test

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}/'.format(thickness,vac))
        slab.to(fmt='poscar', filename='VASP_Files/optB86b-vdW/111_
Slabs/slab_{0}_{1}/POSCAR'.format(thickness,vac))
        optB86bvdW_vasp_files(optB86bvdW_relaxed, input_dir='VASP_F
iles/optB86b-vdW/111_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': r
oot[-2:]}
for k,v in oneoneone_slabs_vaspruns.items():
    v['final_energy'] = v['vasprun'].final_energy
    v['SlabEntry'] = SlabEntry.from_computed_structure_entry(v['vas
prun'].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, oneoneone
thic10_energy), key = lambda t: t[0])
```

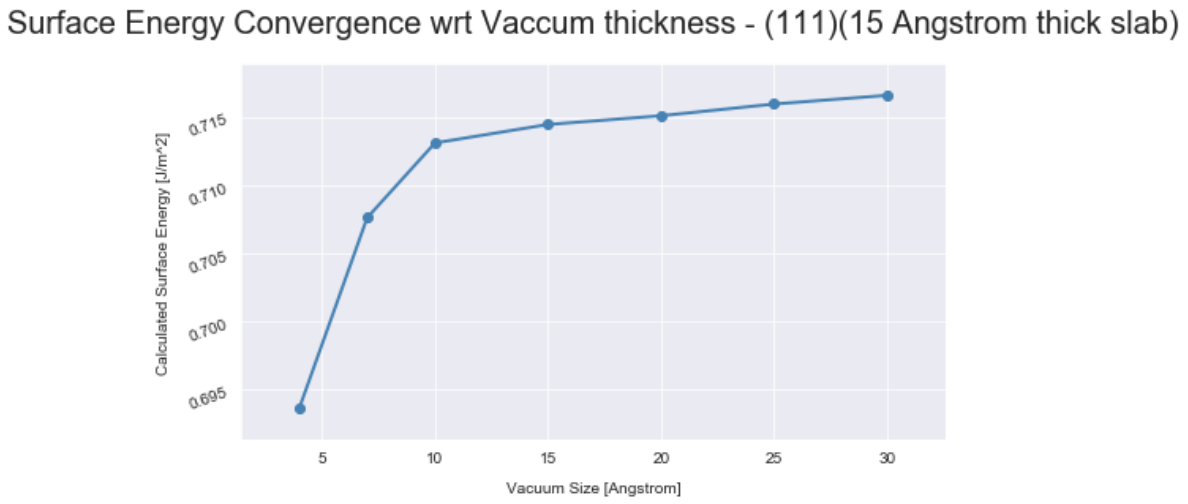
In [32]:
```
f,ax = plt.subplots(1,1, figsize=(8,6))
ax.plot(*zip(*oneoneonethic10), marker="o", linewidth=2, linestyle=
'-', color = 'steelblue')
ax.grid(True)
ax.set_xlabel("Vacuum Size [Angstrom]", labelpad=10)
ax.set_ylabel("Calculated Surface Energy [J/m^2]", labelpad=10)
ax.set_title("Relaxed Slab Surface Energy Convergence wrt Vaccum th
ickness - (111)",
             fontsize=20, pad=20)  # pad is offset of title from p
lot
# 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, oneoneone
thic15_energy), key = lambda 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 p
lot
# 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
```

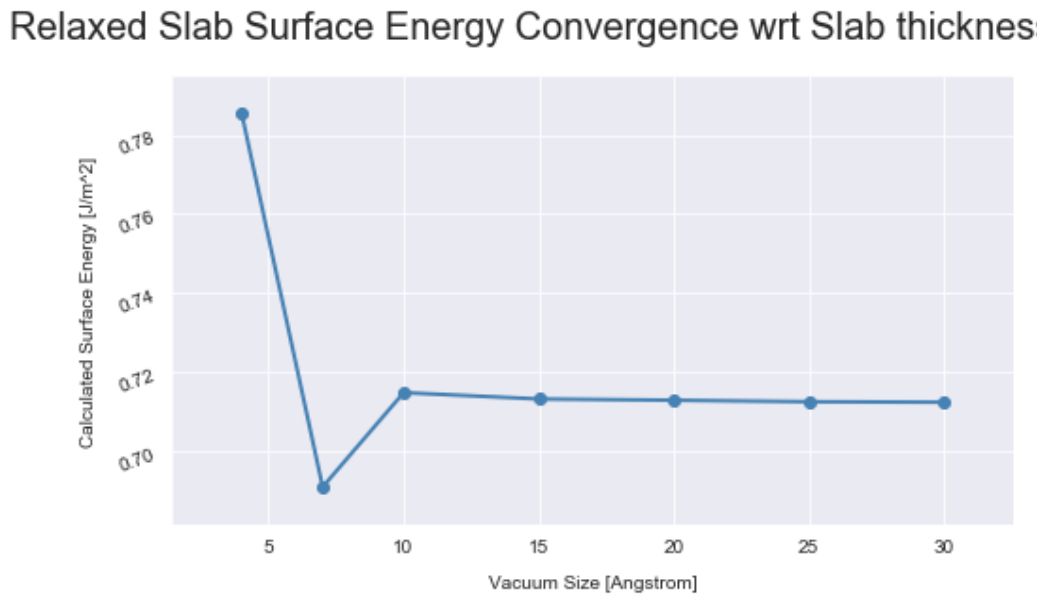


Yep, still converged at 10 Angstrom vac. Let's run convergence test wrt slab thickness, at 10 Angstrom vacuums.

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_Slabs/"):
    for name in files:
        if "vasprun" in name:
            #print(os.path.join(root, name))
            oneoneone_slabs_vaspruns[root[-10:]] = {'vasprun': Vasprun(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 = lambda 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 p
lot
# 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 [ ]: