

Wulff construction and grain boundary in HCP crystals

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Abstract

In this project I have calculated the macroscopic shape of an HCP crystal in zero degrees Kelvin using a Matlab simulation, and calculated the surface energy of two crystals connected in twisted grain boundary and tilted grain boundary, also at zero degrees Kelvin.

Theoretical background

1. Surface tension

When looking at the surface of a liquid or solid matter, we can notice atoms or molecules which have fewer bonds with other atoms or molecules. This causes a force from within the surface that affects the interface with other objects.

Let us define \hat{n} , the normal to a surface element \mathbb{R}^3 :

$$\hat{n} = (\sin(\theta) \cos(\phi), \sin(\theta) \sin(\phi), \cos(\theta)), \quad (1)$$

Let us define $\hat{\epsilon}$, which is the missing bond direction in \mathbb{R}^3 .

A bond will be contained in a unit circle if:

$$b_i(\theta, \phi) = 1, \quad b_i(\theta, \phi) = \begin{cases} 1 & \hat{n} \cdot \hat{\epsilon} > 0 \\ 0 & \hat{n} \cdot \hat{\epsilon} \leq 0 \end{cases} \quad (2)$$

$N(\theta, \phi)$ will be the sum of all bonds contained in a surface element for the same bond energy:

$$N_b(\theta, \phi) = \sum_i b_i \quad (3)$$

The definition of γ is:

$$\gamma(\theta, \phi) = \frac{\sum_b N_b(\theta, \phi) \sigma_b}{\Delta s} \quad (4)$$

Where Δs is a surface element, radius of the circle, and σ_b is the bond energy.

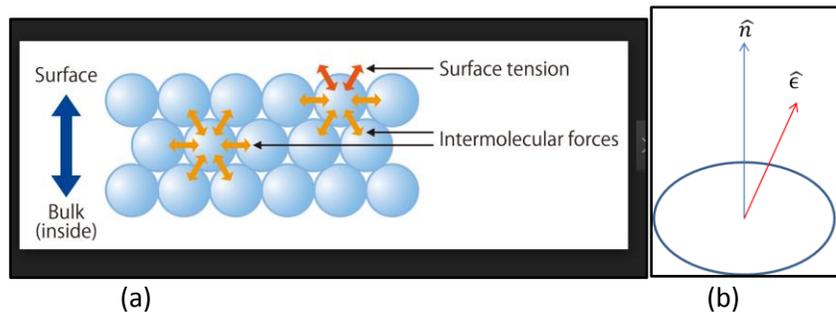


Figure 1: Open bonds. In Figure1 (a) we can see an example of a triangle crystal open bonds^[13]. In figure1(b) we can see a surface element in a shape of a circle and a single bond direction

This potential energy is expressed using the surface tension. The total surface tension energy is,

$$\left(\frac{\partial F}{\partial s}\right)_{T,V} = \gamma, \quad F = \int \gamma ds \quad (5)$$

In Figure 1a we have an example where only the near neighbors' interaction is taken into account, but theoretically we can take as many neighbors as desired, thus increasing our accuracy in describing the surface tension in the trivial case of a lattice with a clear repetitive pattern.

The calculation of the surface tension for a Bravais lattice in zero degrees Kelvin is quite simple, because we can use the symmetric properties of the lattice.

For a Bravais lattice we can describe a point on the lattice by $\vec{R} = n_1 \vec{a}_1 + n_2 \vec{a}_2 + n_3 \vec{a}_3$, where a_1, a_2, a_3 are the primitive vectors and $n_1, n_2, n_3 \in \mathbb{Z}$. That means we can find a set of planes that can describe the lattice, and the open bound of the surface.

The surface tension can be expressed for next near neighbors (NNN) approximation by:

$$\gamma(\theta, \phi) = j_{NN} \sum_{i=1}^{M^{NN}} \sigma_i^{NN} |\hat{\epsilon}_i^{NN} \cdot \hat{n}| + j_{NNN} \sum_{i=1}^{M^{NNN}} \sigma_i^{NNN} |\hat{\epsilon}_i^{NNN} \cdot \hat{n}| \quad (6)$$

Where σ is the number of open bounds in a specific direction, and ϵ is the bound.

For a non Baravis lattice the task is a little trickier because of the lack of basic symmetry, hence we will need to make a numeric calculation.

In my project I have used a model which assumes no “defects” of any sort in the lattice; as well as a static lattice. To describe this, I used Lennard Jones potential between the particles.

$$V \propto \left[\left(\frac{r_m}{r} \right)^{12} - 2 \left(\frac{r_m}{r} \right)^6 \right] \quad (7)$$

Where r_m is the distance at which the potential reaches its minimum.

2. Wulff construction

Definition:

$$U(\partial B) = \int_{\partial B} \gamma(n) ds \quad (8)$$

Theorem: Let W be the Wulff shape for the surface tension function $\gamma(n)$.

Let $B \subset R^d$ be any other region with sufficiently smooth boundary and the same volume as W , then $\tau(\partial B) \geq \tau(\partial W)$, with equality if and only if B and W have the same shape, under the constraint that the volume of B is constant. A proof for this theorem can be found in reference [4]-[5].

The theorem's meaning is that the Wulff shape of the crystal gives the minimal energy solution, and for our case, the physical solution in zero degrees Kelvin.

The Wulff construction is the minimal shape formed by the intersection of all such planes, which are contained in the surface tension's surface.

We can write this term by defining all planes as:

$$L_n = \{x \cdot n \leq \gamma(n)\}, n \in S^{d-1} \quad (9)$$

Where x are all the points on the surface tension's curve.

The Wulff shape is created by taking, for each angle, the plane that has minimal distance from the origin with respect to that angle.

For each point in \mathbb{R}^3 , n takes the form I described at (1)

There are other equivalent ways to describe this construction, which are described in ref [3].

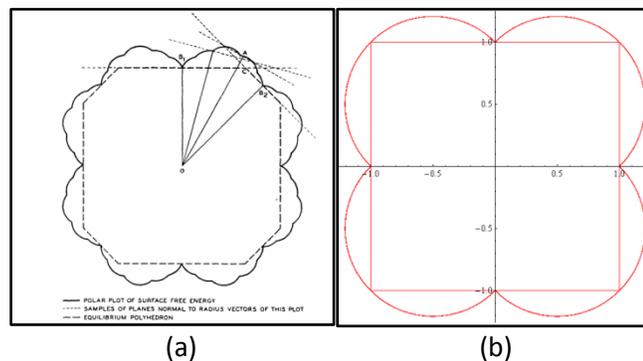


Figure 2: Wulff construction from a surface tension curve: (a) The Wulff construction from a general curve^[4]. (b) The Wulff construction of a cubic square lattice with NN interaction.

3. HCP crystal

A Hexagonal Closed Packed Crystal is created from triangulated planes. We displace every odd plane such that each lattice point of an even lattice is displaced directly above the middle of a triangular in the odd plane underneath it. In the HCP crystal it is customary to use the notation of crystal planes, but instead of using the regular notation of three Miller indices we add an extra index. In the new index system $[hkil]$ the third index is equal to

$$i = -h - k \quad (10)$$

For example, the plane $[110]$ is denoted in the new notation system by $[11\bar{2}0]$. This notation becomes useful when one wants to speak about the HCP symmetries.

In a Helium HCP crystal there are 12 near neighbors and 6 next near neighbors.

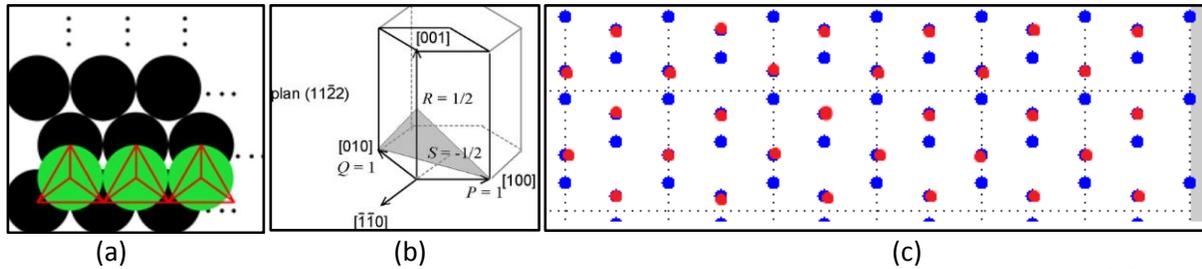


Figure 3: HCP crystal and the four Miller index notation: (a) The construction of an HCP crystal^[11]. (b) An example of the four Miller indices use^[12]. (c) An upper view on the HCP lattice.

Because the HCP lattice is not a Baravis lattice the directions of the bonds are not identical for all atoms. Each atom has 12 NN, 6 of them in the same z coordinate creating a hexagon, while the other 6 are not in the same z coordinate.

Let us choose an atom in the HCP lattice and denote its bonds vector \vec{B} . For each atom on the lattice the bond vector is either \vec{B} or $-\vec{B}$.

4. Grain boundary

Thus far we focused on the shape of the crystal at zero degrees Kelvin. However in solid matter such shapes rarely take place. Instead we have scatter with many crystal domain, where each crystal is cut and connected to the other crystal in different orientations. This connecting interface is called the Grain boundary.

For describing effectively this connection, let us use a notation including the first crystal's axis system, the axis of the interface, and their relative orientation using the rotation angle θ :

$\theta^\circ [h_0, k_0, l_0], (h_{nA}, k_{nA}, l_{nA})$. Another, more convenient way to describe the grain boundary is to use $\theta^\circ [h_0, k_0, l_0], (h_{nA}, k_{nA}, l_{nA}) / (h_{nB}, k_{nB}, l_{nB})$. This method gives us a clearer view on how the crystals are connected.

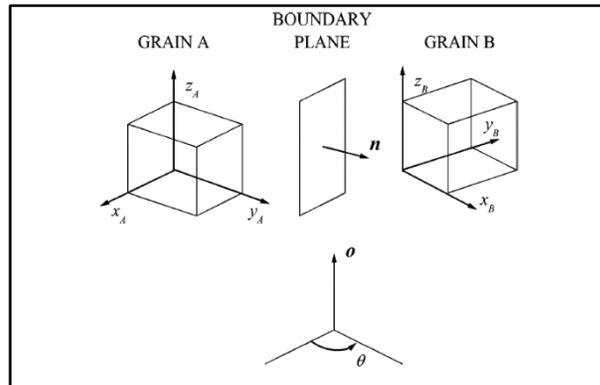


Figure 4: A description of grain boundary parameters^[8]

Let us now discuss two types of grain boundaries: the tilted grain boundary and the twisted grain boundary.

The twisted grain boundary characterizes attaching both crystals in the same orientation and then rotating one of them so that the connecting plane boundary "plane normal" is not changed.

The tilted grain boundary characterizes attaching both crystals in the same orientation and then rotating both by an angle θ and $-\theta$ such that the boundary plane is fixed.

Low angle grain boundary for the case of the tilted grain boundary can be expressed in a simple theoretical way.

We can define vectors D and b , where D is the dislocation spacing (the distance between two repeatable atoms) and b is twice the orthogonal projection of the distance between the two planes onto the boundary plane (as described in figure 5).

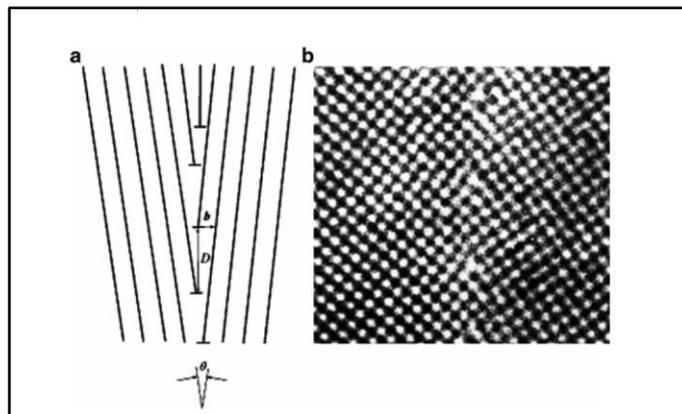


Figure 5: The connected plane and parameters of tilted grain boundary^[8]

So the relation between the tilted angle, D and b is:

$$\sin\left(\frac{\theta}{2}\right) = b/2D \quad (11)$$

In the small angle approximation we get:

$$\theta = \frac{b}{D} \quad (12)$$

And we can further develop this to get the relation between the surface energy per area and the angle as:

$$\sigma = \gamma_0 \theta (A - \ln \theta) \quad (13)$$

where

$$\gamma_0 = \frac{Gb}{4\pi(1-\nu)} \quad , \quad A = 1 + \ln\left(\frac{b}{2\pi r_0}\right) \quad (14)$$

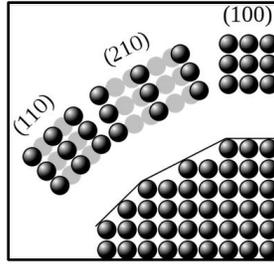
G is the shear modulus, a measurement to the stiffness of the material.

ν is Poisson's ratio, a measurement to tendency of the material to expand while it is being compressed.

r_0 is the radius of the dislocation core.

(For further explanations see [7])

In the grain boundary in particular, it is sometimes worthwhile to consider the crystalline planes, which are the planes that connect a group of atoms together, as illustrated in figure 6.

Figure 6: The crystal planes^[12]

Codes

In some of the visualization I have used AViz^[14]. All the distances and energies are normalized. In order to get the scale distances and energies one need to multiply by the by the NN bond energy divided by the distance between two atoms in the lattice or in the NN bond energy.

In all the graphs are plotted in the Cartesian coordinate system ($[x,y,z]$) unless mentioned otherwise.

1. Gidi Baum's code for calculating surface tension in HCP crystals- Fortran^[7]

This code receives the number of particles NL , and uses it to create a reference frame of a crystal in the size of $2NL \times 2NL \times 2NL$. The program runs for $\left\{ \theta: [0, \pi], \phi: \left[0, \frac{2\pi}{3} \right] \right\}$. For each angle it calculates the suitable \hat{n} . For each atom that is close to the surface (for calculating NN or NNN interaction) it calculates the number of open bounds, multiplying the stable interaction energy (calculated from Lennard Jones potential) and dividing it by the area of the surface. There are two codes, one for NN and another for NNN approximation. I only used the NNN approximation.

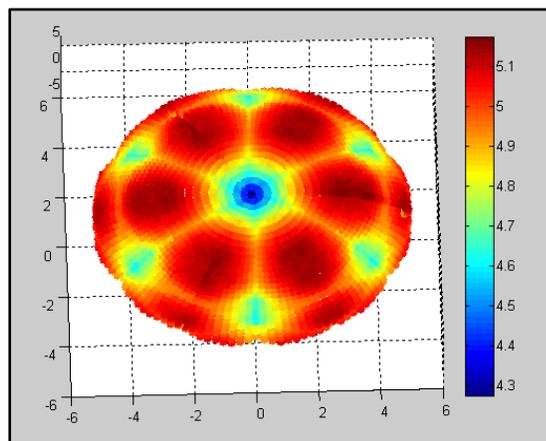


Figure 7: The surface tension surface for $NL = 50$. The colors represent the distance from the origin. The axes are in the Cartesian coordinate system.

2. Wulff construction code- Matlab (Original)

This code can plot a general Wulff construction when given a surface tension surface. For each point n on the surface tension it builds the plane:

$$z_{plain_i} = -(\sin(\theta_j) \cos(\phi_k) * x_i + \sin(\phi_k) \sin(\theta_j) * y_i)/d \quad (15)$$

$$d = -(x_n, y_n, z_n) \cdot (\sin(\theta_j) \cos(\phi_k), \sin(\phi_k) \sin(\theta_j), \cos(\theta_j)) \quad (16)$$

The program minimizes r for all different planes and is used for getting the minimal shape, the Wulff construction. This program can create from a general numeric surface tension curve its Wulff shape (by changing the required parameters, like θ and ϕ).

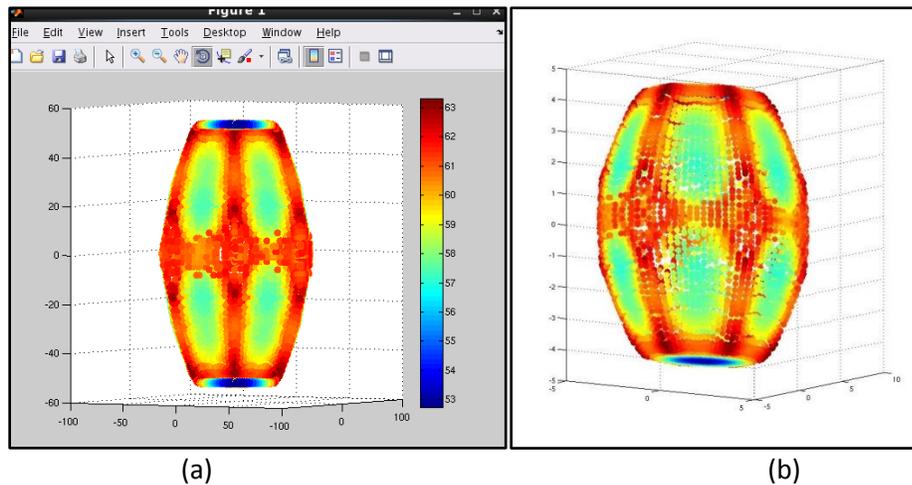


Figure 8: The Wulff construction of a crystal for $NL = 50$. In (a) we can see the crystal features up to scale. In (b) the crystal is not scaled. For getting the proper scale one need to use (3). The axes are in the Cartesian coordinate system.

3. Creating HCP crystal in 0^0K - Matlab (original code beside Inhull function from Matlab files exchange. written by John D'Errico)^[15]

This code is given the number of particles NL and the Wulff shape of the lattice. The code constructs a model of $(2NL + 10)^3$ particles and generates its Wulff shape with a 0.5% error. The code iteratively checks how many points of the lattice are inside the Wulff shape. If the error is bigger than 0.5% it shrinks or expands the Wulff shape.

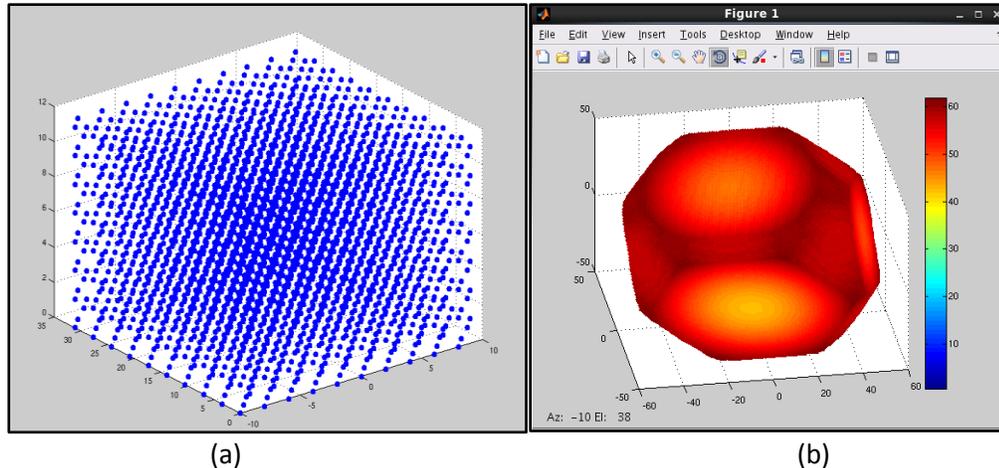


Figure 9: Contracting an HCP crystal. In (a) there is an example of a $2NL \times 2NL \times 2NL$ bulk. (b) is the Wulff shaped crystal in size $NL = 50$. The axes are in the Cartesian coordinate system.

4. Cutting, Rotating and Connecting Crystals Interface- Matlab GUI (original)

This graphic user interface can receive one or two txt files of lattice points. The code then generates the crystal, and the user can cut, rotate and shift each crystal. The user can also plot both crystals on the same axis. The user can then create a xyz file for each new crystal and for both crystals together.

5. Calculating the free energy for an area unit (NN approximation) – Matlab (original)

This code receives both crystals xyz file and calculates the surface energy using a model which approximates the missing bonds.

Since we twisted or tilted the crystals one against the other, we in fact broke the crystal's structure (now referring to the two crystals as one bicrystal). We now ask ourselves, how can we count the open bonds and calculate the surface tension if the unit cell of the crystal does not exist in the boundary?

To overcome this problem I have used a model that finds all neighbors (in NN approximation) and approximates them (if necessary) to the nearest orientation from its original bonds.

The approximation is being done by calculating the projection of the original bonds on each of the existing bond between one crystal to itself and between the two crystals. If the biggest projection is bigger than a threshold value the user can determine, the bond is counted as a close bond.

After that it is easy to complete the orientation of the missing bonds. The code then counts all the open bonds and divide this result by the surface area.

I have related to two boundary conditions: infinite boundary condition and finite boundary condition. In the infinite boundary condition I ignored the effect of the outer contour surface by taking a surface element of a circle that all the atoms which are the closest to its circumference from the inside of the circle are connected to other atoms from without the circle.

In the finite boundary conditions I have used all the atoms on the plane for the calculation.

For infinite boundary condition it is a circle in the size I had used for the calculation, and in finite boundary conditions it is the finite surface area which I've calculated using triangulation summation.

In all the calculation I've used the distance of the new bonds to be no more than 1.01 in normalized units. This also can be changed by the user.

Results:

1. Wulff construction in HCP crystals

I got Wulff's shape of several models, from $NL = 20$ to $NL = 50$.

It is clearly shown that as there is a numeric error in the graphs plotting, but it decreased as lattice is bigger.

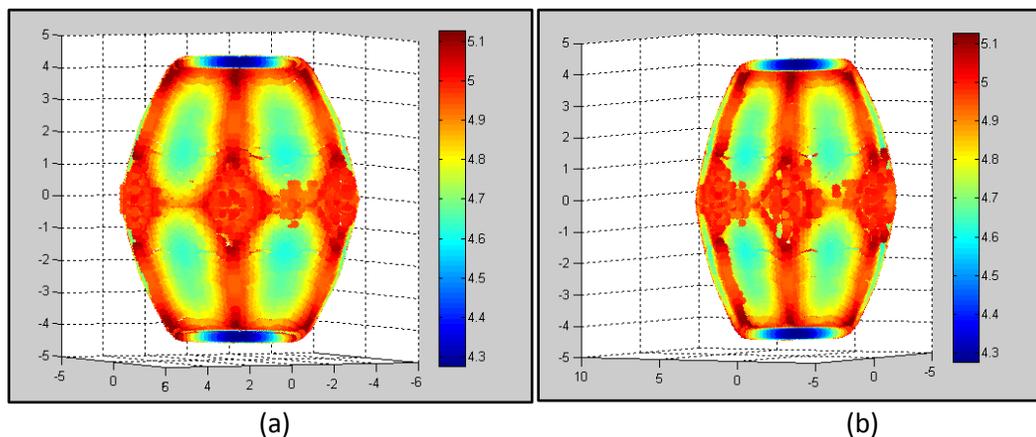


Figure 10: The Wulff construction of (a) $NL = 40$ and (b) $NL = 20$. The axes are in the Cartesian coordinate system.

2. The Twisted grain boundary:

In all the grain boundary simulations I have used the $NL = 50$ model. In this part I had cut two crystals, one above the $z = 0$ plane and one below $z = 0$ plane and twisted one relatively to the other (around the z axes) in 1 degree jumps ($\theta \in [0,17]$)

a. Infinite boundary conditions

In this calculation I've taken the circle radius to be $r = 30$. In that way I eliminated the boundary effect.

To try and estimate what will be the best threshold to estimate if a bond is "close enough" to one of the original bonds, I've run this simulation with 2 possible thresholds 0.5 and 0.85.

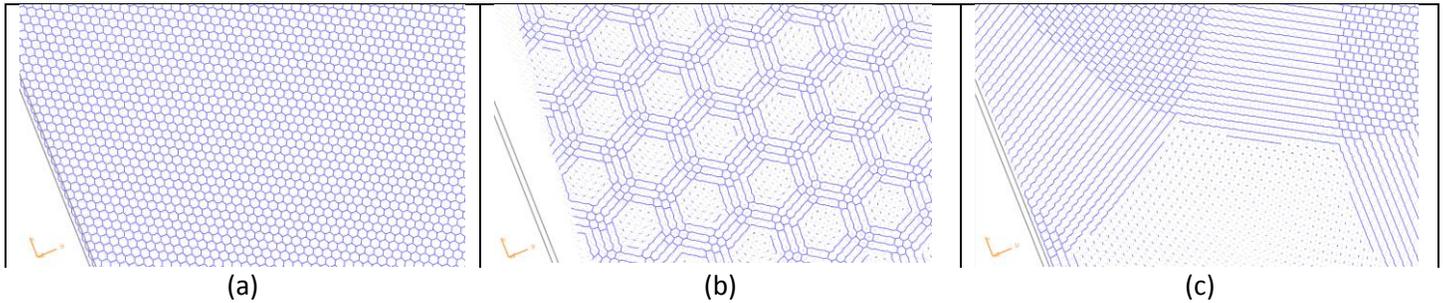


Figure 11: Bonds of twisted grain boundary between the two planes in bond constrained to the maximal length of 1.1: (a)- not rotated, (b) – rotation of 2 degrees, (c) rotation of 7 degree. The pattern in the 2 degrees split but conserve. The photos are in scale and in the same axis direction.

b. Finite boundary limit

In order to check the effect of the crystals boundary I took $r = 120$. This obviously will reduce the calculated energy, so the result will indicate the qualitative behavior of the energy.

As we can see in both results the surface energy is zero or very close to zero when the rotation is zero.

In the infinite case the surface energy is constant, that is because the number of bonds don't change a lot while rotating, and in each degree some bonds close while other opens. In the finite limit we see a slow increase in the energy, due to the rotation which exposes the atoms.

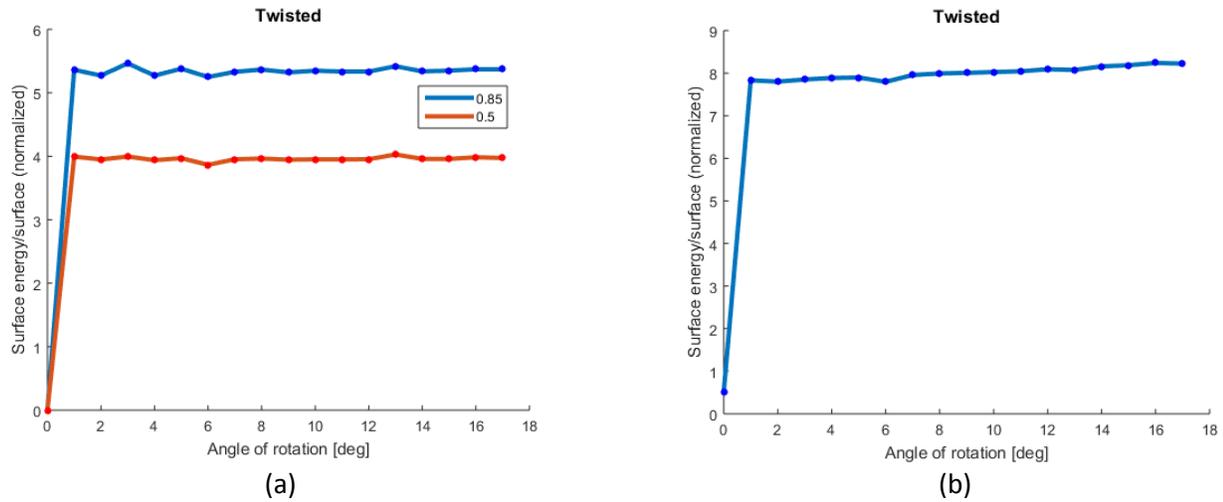


Figure 12: Results for infinite and finite boundary conditions. In graph (a) the calculation was performed on 2 thresholds: 0.5 and 0.85. In graph (b) was calculated for threshold = 0.5. Notice that the graph doesn't start from zero, due to the boundary term, and that the scale of energy is a little bigger. That is due to the rotation, which is exposing more atoms which are now taking into consideration.

3. The tilted grain boundary

In this part I had twisted both crystals around the x axis, the first in θ and the second in $-\theta$, and cut them in $z = 0$ plane. I simulated with infinite boundary conditions.

The results indicate a strong dependency on the angle, as expected.

As the angle increase fewer bonds are forming due to the high change from the original orientation of the crystal.

I've calculated this dependency with 0.5 threshold.

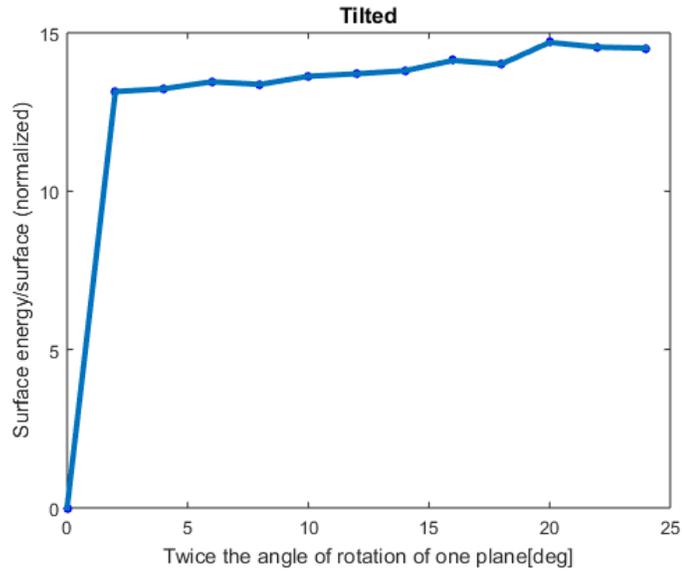


Figure 13: Tilted grain boundary curve.

Numerical errors:

All the values given in this report have a numerical error due to that a lot of the sizes are given by irrational numbers can only be approximated by a finite number of digits. That can refer to the places of the atoms in the lattice, the value of numbers after been operated with trigonometric function or inverse trigonometric function. These errors can effect on the number of atom which are inside a surface element and the result of a dot product, which affects digits after the zero in the surface energy calculations.

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Pictures are from the Reference list and:

11. https://en.wikipedia.org/wiki/Close-packing_of_equal_spheres
12. https://en.wikipedia.org/wiki/Miller_index
13. http://www.face-kyowa.co.jp/english/en_science/en_theory/en_what_Surface_tension/

For visualization I have used AViz:

14. <http://phycomp.technion.ac.il/~aviz/>

The inhull function from Matlab file exchange.

15. <http://www.mathworks.com/matlabcentral/fileexchange/10226-inhull>