Chemistry 801: *Nanostructured Materials and Interfaces*

Problem set 1: Answer key

1. For a perspective on surface-to-volume ratio, consider a sphere whose radius is 1 cm and determine its surface area and volume. If the sphere is now subdivided into identical spheres, whose radii are each 1 nm, how many spheres will there be if the total volume of the original large sphere is preserved in the collection of nanospheres? Determine the collective surface area of these nanospheres.

Answer:

The surface area of a sphere is 4*pi*r^2. For a sphere of radius 1 cm, this makes a surface area of 12.6 cm^2. The volume of a sphere is 4/3*pi*r^3, giving a volume of this same sphere of 4.20 cm^3. Now subdivide into nanospheres of radius 1 nm. In linear dimensions, the nanospheres are smaller by a factor of 10^7, so that in terms of volume, 10^{21} of them will have the same volume as one sphere of radius 1 cm. Now each of the nanospheres has an area of 12.6 nm^2. This is 12.6 * 10^{-18} m^2. Multiply by the number of nanospheres to give their collective surface area: 1.26×10^4 m^2, which is about three acres, or 10^7 times greater than the surface area of the one sphere of radius 1 cm.

In heterogeneous catalysis, catalytic activity typically scales with the surface area of the solid catalyst. This exercise shows why nanoparticles of catalyst are so often used: maximum activity (surface area) with minimum amount (volume) of catalyst.

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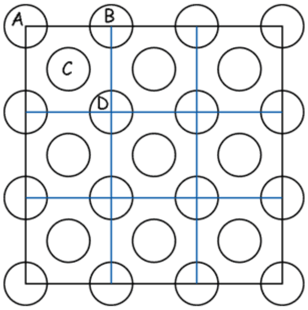
2. Prepare a table like that presented in class for BCC unit cells for face-centered cubic (FCC) unit cells. Your table should list numbers of surface and interior atoms as a function of cube size up to the size at which there are more interior than surface atoms. For the element Au with a unit cell edge length of about 4 Å, at about what size does the number of interior atoms exceed those on the surface?

Answer:

One way to approach this problem is to draw out the cubes whose linear dimensions n are some small number of unit cells (up to n = 3), then try to generalize algebraically. First, let's try counting the surface atoms. Below is shown one face of a cube where n = 3. The blue lines indicate the boundaries between unit cells.



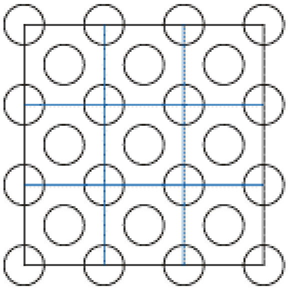
To make counting easier and less prone to mistakes, take advantage of the symmetry. One can divide the atoms into four groups, as shown on the above diagram. Group A is the atoms on the corners of the face. Group B is those on the edges. Group C is the atoms in the center of each unit cell, and group D comprises those on the intersections of the blue lines representing unit cell boundaries. The next step is to count them, first for the particular case of $n = 3$, then for the general case, where n is any positive integer. The results are as follows:

- Group A: For $n = 3$, there are four atoms shown on the diagram. Because they are on the corners, each is shared among three adjacent faces. This makes 4/3. Now multiply by six faces to obtain 8 atoms. As a check, note that a cube has eight corners. To extend this to the general case, every cube will have the same number of corners no matter how large it is, so in general there are 8 atoms in group A.
- Group B: There are eight atoms shown on the diagram. They are on an edge, so each is shared among two faces; this makes 4. Multiply by six faces to get 24 atoms. As a check, a cube has twelve edges, with two atoms on each edge in this case. To extend to the general case, note that the atoms are located on the intersection between the blue lines and the edges. Each edge has $n-1$ blue lines. Multiply by the number of edges to obtain $12(n-1)$.
- Group C: There are nine atoms shown on the diagram. They are not on corners or edges, so there is no sharing factor by which to divide. Six faces make 54 total atoms. Inspection will quickly reveal that the number of atoms on each face is n^2, making $6n^2$ total.
- Group D: The diagram shows four atoms on the face, no sharing, so there are 24 total. Note that they are all located on the intersections of blue lines. As noted above, there are $n-1$ blue lines in both the horizontal and vertical directions, so there must be $(n-1)^2$ intersections. Total for group D: $6(n-1)^2$.

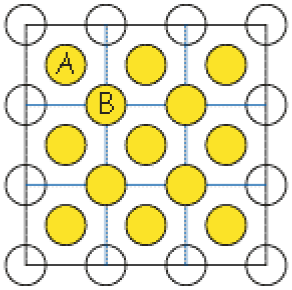
Now find the sum of the four groups and simplify algebraically. The final result is:

$12n^2 + 2$ atoms on the surface.

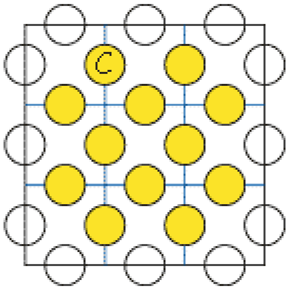
Counting interior atoms is somewhat more involved because of the three-dimensional nature. A good way to simplify it is to use a layer diagram such as the one shown below, again for the cube of linear dimensions n = 3.



z = 0, 3



z = 1, 2



z = 0.5, 1.5, 2.5

The vertical dimension, z, is given in units of n. z = 0 and 3 are the bottom and top layers, so no interior atoms are there. As for the rest, the yellow atoms in each layer are counted because they represent interior atoms, and these can be divided into three groups, as shown above. One must also take into consideration the number of layers, which varies linearly with n, except for the top and bottom layers (which contain no interior atoms). There is no sharing, because layers do not intersect. The atoms in the three group are counted as follows:

Group A: There are nine in the layer shown, and there are two such layers to give a total of 18. To extend this to the general case, each atom is in the center of the small square representing the unit cell, making n^2 per layer. There are n-1 layers, because they are found at the integral z values, and we must discount the top and bottom. This gives a total of $n^2(n-1)$ atoms in Group A.

Group B: These are found on the intersections of the blue lines. This situation was encountered previously when counting group D of the surface atoms; there are $(n-1)^2$ of them per layer here. Again, there are n-1 layers, so the total is (n-1)(n-1)(n-1).

Group C: There are twelve shown per layer. To extend this to the general case, notice that they are found on the blue lines, but not at the intersections. Each blue line has n of them, and there are 2(n-1) blue lines total. This makes 2(n-1)n atoms per layer. To count these layers, note that in this case there are three of them; each is midway through each unit cell. This makes n layers total, giving $2(n-1)n^2$ atoms in group C.

Total the atoms in all the groups and simplify algebraically. Final result:

$$4n^3-6n^2+3n-1 \text{ interior atoms}$$

Once this algebraic expression has been found, a spreadsheet is well suited for calculating the numerical values.

n	surface atoms	interior atoms	surf./int. ratio
1	14	0	!div by zero!
2	50	13	3.85
3	110	62	1.78
4	194	171	1.13
5	302	364	0.83
6	434	665	0.655
7	590	1098	0.535
8	770	1687	0.455
9	974	2456	0.395
10	1202	3429	0.350
11	1454	4630	0.314
12	1730	6083	0.284
100	120,002	3,940,299	0.0304
1000	12,000,002	3,994,002,999	0.00300

The switchover point in terms of surface/interior ratio is between n = 4 and 5. For gold, this corresponds to a cube length of between 1.6 and 2.0 nm.

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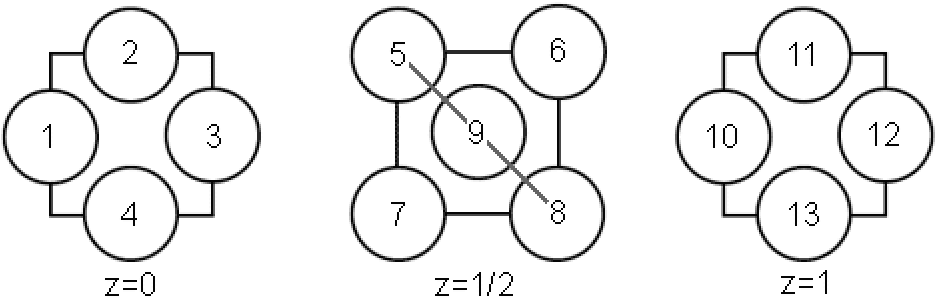
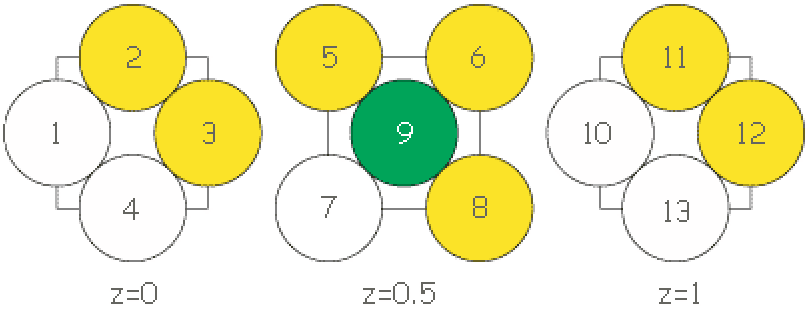
3. Consider the layer sequence shown below that defines a FCC unit cell. Which atoms are nearest neighbors of atom 9? The diagonal line indicates the direction of a (110) plane. Which numbered atoms are removed and which remain to define the (110) plane containing atom 9?



Answer:

All the atoms in the diagram (except 9 itself) are nearest neighbors of number 9, and all the nearest neighbors of number 9 are shown in the diagram. Shown below is the diagram redrawn, with the circles representing the atoms scaled so that the ones that should be touching are shown that way.



The green atom is number 9. Take out everything below and to the left of the diagonal line in the first figure, and the result is shown as white circles for missing atoms and yellow for those that are still present. Seven of the twelve neighbors are still there; five are missing.

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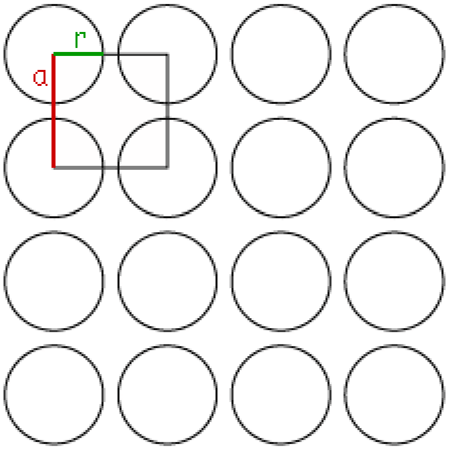
4. Considering the favorable nature of surface close packing, which of the three BCC low-index planes – (100), (110), or (111) – do you expect to have the lowest surface energy and why?

Answer:

If we consider only the surface packing efficiency, the following analysis results:

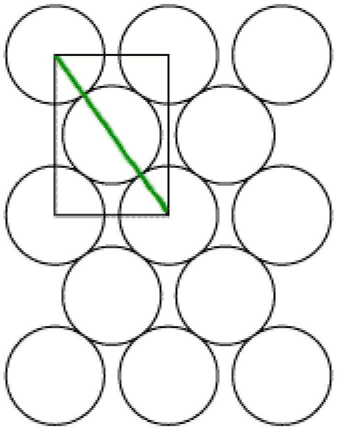
(100) plane: The area covered by a circle is pi*r^2. The linear dimension, a, of a bcc unit cell is the same as the linear dimension of the square unit cell that makes up the (100) surface.



The body diagonal of the bcc unit cell is 4r. Also, the body diagonal is sqrt(3) times a. Therefore, a = (4/sqrt(3))r. The area covered by the (100) surface unit cell is a^2. It contains 4/4 = 1 atom. Numerically:

- area covered by atoms (circles): 3.14 r^2.
- total area of unit square: 5.33 r^2.
- ratio (packing efficiency): 58.9 %

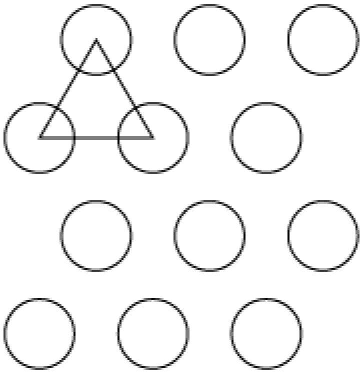
For the (110) plane, the unit cell is a rectangle of dimensions a and the face diagonal, sqrt(2)*a. Again, the body diagonal (the (110) plane contains the body diagonal) is 4*r (see green line in diagram below):



In terms of r, the unit rectangle dimensions are (4/sqrt(3))*r and (4*sqrt(2)/sqrt(3))*r, area (16*sqrt(2)/3)*r^2. The rectangle covers two atoms, so the surface area covered by them is 2*pi*r^2. Numerically, then,

- Area covered by atoms (circles): 6.28*r^2
- Total area covered by rectangle: 7.54*r^2
- Ratio (packing efficiency): 83.3 %

The (111) plane is the most difficult to visualize. Imagine turning a bcc unit cell such that one vertex is on the top and one is on the bottom. The (111) plane passes horizontally through the central atom. The six vertices around the "equator" of the central atom are actually in a puckered, six-membered ring. Therefore, the central atom is the only one in the unit cell that is on the (111) plane. The diagram below shows the (111) plane, again with the atoms drawn to scale:



Note that this plane is quite loosely packed. To calculate how loosely, realize that each side of the triangle in the above diagram is a face diagonal, which is [(4*sqrt(2))/sqrt(3)]*r. This is the base dimension. The height is 2*sqrt(2)*r. This makes the area of the triangle equal to [8/sqrt(3)]r^2, or numerically, 4.62*r^2. The triangle contains 3/6 or 1/2 an atom, numerically 1.57*r^2, making for a packing efficiency of only 34.0%.

From these calculations (and one can see it visually in the diagrams), it is clear that the (110) plane has the closest packing. This gives it the lowest energy, because it has a maximum number of nearest neighbors along the surface, minimizing the number of bonds that must be broken to cleave at that surface.

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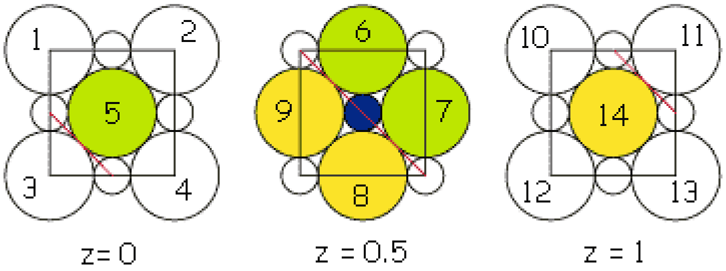
5. How many anion nearest neighbors are missing from the cations on the surface of the (111) planes in rock salt? Illustrate your answer with a layer sequence in which you number atoms to identify them.

Answer:

Shown below is a layer sequence for sodium chloride.



The blue circle represents the cation being considered. The colored large circles are the six anions that surround it, numbers 5, 6, 7, 8, 9, and 14. The red line shows where the (111) plane crosses each layer. Everything below and to the left of this has been removed, as indicated by yellow instead of green. This leaves three of the six nearest neighbors missing; the missing ones are 8, 9, and 14.