Department of Materials Science and Engineering
Norwegian University of Science and Technology

TMT4320 Nanomaterials, fall 2015

EXERCISE 1 - SOLUTION

PROBLEM 1

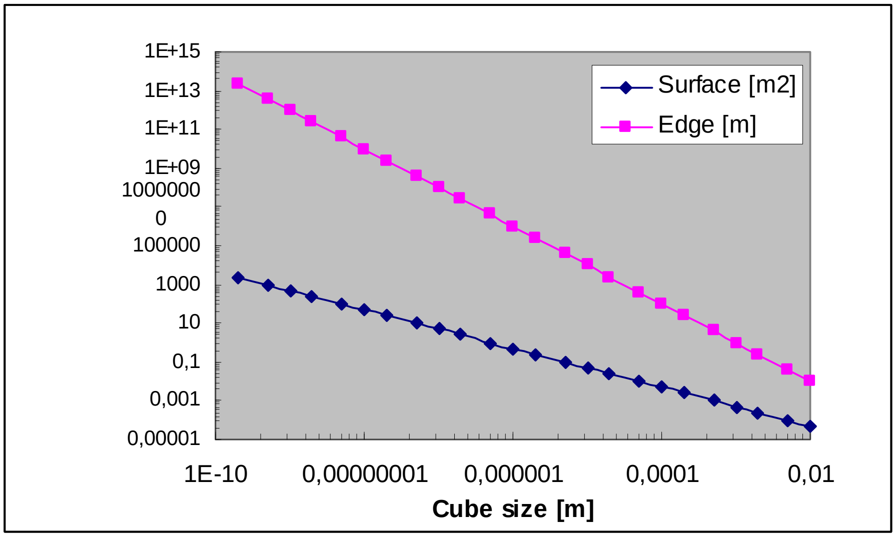
a) Volume of 1 g Pd:
$V = m/\rho = 1/12\ \text{cm}^3 = 8.3\times10^{-8}\ \text{m}^3$

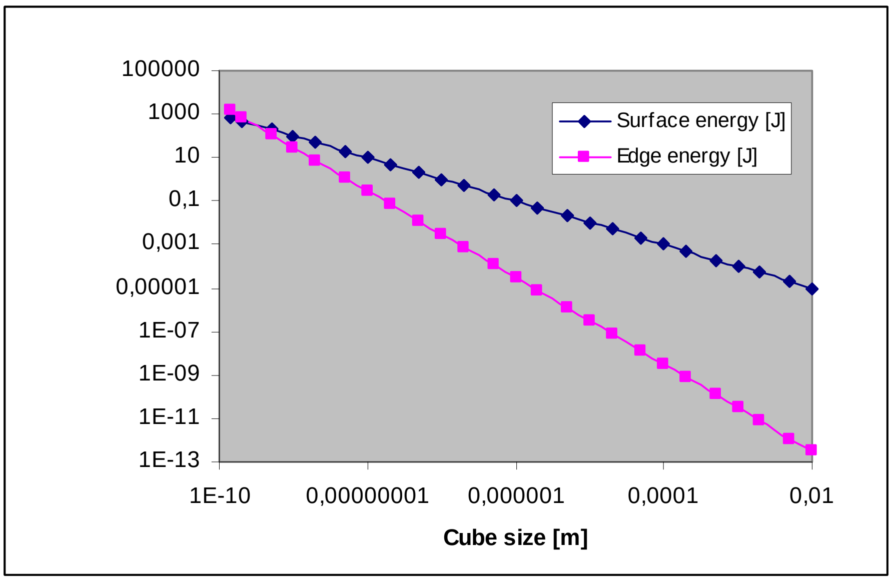
The number of cubes (n) with size a is given by V divided by the volume of the cube (V_c):
$n = V/V_c = V/a^3$

The total surface of the cubes: $A = n\cdot6\cdot a^2 = (V/a^3)\cdot6\cdot a^2 = 6V/a$
The total length of the edges of the cubes: $L = n\cdot12\cdot a = V/a^3\cdot12\cdot a = 12V/a^2$

The total surface energy of the cubes: $E_A = 6V/a\cdot2\times10^{-5}\cdot100^2$ J
The total energy of the edges of the cubes: $E_L = 12V/a^2\cdot3\times10^{-13}\cdot100$ J

a [m]	n	A [m^2]	L [m]	E_A [J]	E_L [J]
0,01	0,083333333	0,00005	0,01	0,00001	3E-13
0,005	0,666666667	0,0001	0,04	0,00002	1,2E-12
0,002	10,41666667	0,00025	0,25	0,00005	7,5E-12
0,001	83,33333333	0,0005	1	0,0001	3E-11
0,0005	666,6666667	0,001	4	0,0002	1,2E-10
0,0002	10416,66667	0,0025	25	0,0005	7,5E-10
0,0001	83333,33333	0,005	100	0,001	3E-09
0,00005	666666,6667	0,01	400	0,002	1,2E-08
0,00002	10416666,67	0,025	2500	0,005	7,5E-08
0,00001	83333333,33	0,05	10000	0,01	3E-07
0,000005	666666666,7	0,1	40000	0,02	1,2E-06
0,000002	10416666667	0,25	250000	0,05	7,5E-06
0,000001	83333333333	0,5	1000000	0,1	0,00003
5E-07	6,66667E+11	1	4000000	0,2	0,00012
2E-07	1,04167E+13	2,5	25000000	0,5	0,00075
1E-07	8,33333E+13	5	1E+08	1	0,003
5E-08	6,66667E+14	10	4E+08	2	0,012
2E-08	1,04167E+16	25	2,5E+09	5	0,075
1E-08	8,33333E+16	50	1E+10	10	0,3
5E-09	6,66667E+17	100	4E+10	20	1,2
2,00E-09	1,04167E+19	250	2,5E+11	50	7,5
1,00E-09	8,33333E+19	500	1E+12	100	30
5,00E-10	6,66667E+20	1000	4E+12	200	120
2,80E-10	3,79616E+21	1785,714	1,28E+13	357,1429	382,6531





The enthalpy of vaporization of Pd is 362 kJ·mol^{-1}. The vaporization energy of 1 g Pd is 3400 J. The surface and edge energy does not become significant compared to the vaporization energy before the size is below 100 nm.

The atomic radius of Pd is 0.14 nm. The sum of the edge energy and surface energy when *a* = 0.14 nm is 2245 J in good accordance with the enthalpy of vaporization meaning that all the Pd atoms are not bonded to any other atom.

Note that the surface energy correspond to a relaxed surface and at sufficiently small size the surface energy become dependent on size and the calculation performed here will have a significant error.

b) The number of spheres (n) with diameter a are given by V divided by the volume of the sphere (V_s):

$$n = \frac{V}{V_{\text{sphere}}} = \frac{V}{\frac{4}{3}\pi\left(\frac{a}{2}\right)^3} = \frac{6V}{\pi a^3}$$

The total surface of the spheres: $A = n \cdot 4\pi\,(a/2)^2 = 6V/a$
The total surface energy of the spheres: $E_A = 6V/a \cdot 2\times10^{-5} \cdot 100^2$ J

a [m]	n	A [m^2]	E_A [J]
0,01	0,159235669	0,00005	0,00001
0,005	1,27388535	0,0001	0,00002
0,002	19,9044586	0,00025	0,00005
0,001	159,2356688	0,0005	0,0001
0,0005	1273,88535	0,001	0,0002
0,0002	19904,4586	0,0025	0,0005
0,0001	159235,6688	0,005	0,001
0,00005	1273885,35	0,01	0,002
0,00002	19904458,6	0,025	0,005
0,00001	159235668,8	0,05	0,01
0,000005	1273885350	0,1	0,02
0,000002	19904458599	0,25	0,05
0,000001	1,59236E+11	0,5	0,1
5E-07	1,27389E+12	1	0,2
2E-07	1,99045E+13	2,5	0,5
1E-07	1,59236E+14	5	1
5E-08	1,27389E+15	10	2
2E-08	1,99045E+16	25	5
1E-08	1,59236E+17	50	10
5E-09	1,27389E+18	100	20
2,00E-09	1,99045E+19	250	50
1,00E-09	1,59236E+20	500	100
5,00E-10	1,27389E+21	1000	200
2,80E-10	7,25381E+21	1785,714	357,1429

Note that the total surface area and total surface energy are equal for cubes and spheres at the same particle size a. This is because the surface area/volume ratios of a sphere with diameter a and a cube with side length a are equal ($6/a$). The number of cubes and spheres are different though. (NB: The surface area of a sphere is of course smaller than that of a cube with the same volume. See d).

c) At small sizes one may calculate the fraction of surface atoms from table 1. The atoms are close-packed in an fcc lattice. The palladium atomic radius (R) is 0.14 nm (0.14×10^{-9} m).

Cluster size [atoms] = 1 + 2 × number of shells (number of atoms across diameter)
Cluster size [m] = cluster size [atoms] × $2R$ (diameter in meters)

Shells	Cluster size [atoms]	Cluster size [m]	Surface atoms [%]
0	1	2,8E-10	100
1	3	8,4E-10	92
2	5	1,4E-09	76
3	7	1,96E-09	63
4	9	2,52E-09	52
5	11	3,08E-09	45
7	15	4,2E-09	35

For larger sizes we can make an estimate by assuming a monolayer of atoms at the surface.
The total number of atoms in 1 g Pd:

$N_{tot} = N_A/M_{m,Pd} = 6.022\times10^{23}/106.4 = 5.65977\times10^{21}$

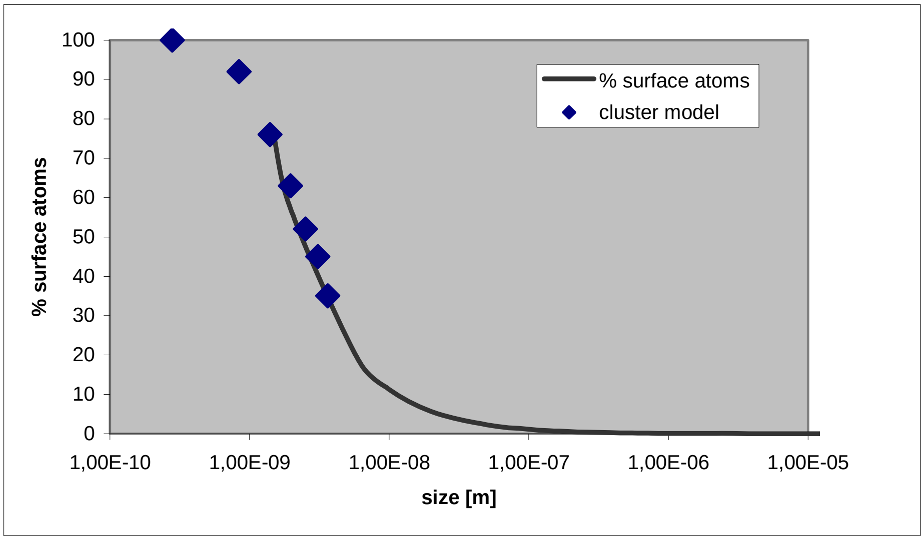
The surface is assumed to correspond to a monolayer of atoms with radius R=0.14 nm.
Each atom is assumed to cover a surface equal to a square with size $2R\times2R$ ($4R^2$).
The surface area of the spheres (A) are calculated as in b).
The number of surface atoms are:

$$N_{\text{surface}} = \frac{A}{4R^2} = \frac{\frac{6V}{a}}{4R^2} = \frac{3V}{2R^2 a}$$

The relative amount of surface atoms is then given by:

$$\%\text{ surface atoms} = \frac{N_{\text{surface}}}{N_{\text{tot}}}\times100\% = \frac{\frac{3V}{2R^2 a}}{N_{\text{tot}}}\times100\% = \frac{3V}{2R^2 a N_{\text{tot}}}\times100\%$$

a [m]	Surface atoms [%]
0,01	0,00001
0,005	0,00002
0,002	0,00006
0,001	0,00011
0,0005	0,00023
0,0002	0,00056
0,0001	0,00113
0,00005	0,00225
0,00002	0,00563
0,00001	0,01127
0,000005	0,02254
0,000002	0,05634
0,000001	0,11268
5E-07	0,22536
2E-07	0,56341
1E-07	1,12682
5E-08	2,25364
2E-08	5,63410
1E-08	11,26821
5E-09	22,53641
2E-09	56,34104
1E-09	112,68207
5E-10	225,36414
2,8E-10	402,43597



We see that the two models overlap well in the 1.5-4 nm region.

d) The radius of a sphere with the same volume as a cube with edge *a*:

$4/3\ \pi R^3 = a^3$

$R = (3/4\pi)^{1/3} a = 0.62a$

The surface of the sphere: $4\pi(0.62a)^2 = 4.84a^2$
The surface of the cube: $6a^2$

The surface of the sphere is 80% of the surface of a cube with equal volume. Spheres are the object with the lowest surface area per volume.

e) Average surface energy of the nanowires = ½ [1.41 x 1.23 + 1.22 x 1.23] = 1.62 $\mathrm{Jm^{-2}}$