DETERMINATION OF THE SURFACE FREE ENERGY OF METALLIC NANOPARTICLES

BY

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SUBMITTED TO DEPARTMENT OF PHYSICS,
FACULTY OF PHYSICAL SCIENCES
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IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE AWARD OF BACHELOR OF SCIENCE (B.Sc.) IN INDUSTRIAL PHYSICS

FEBRUARY 2025

CERTIFICATION

This is to certify that this project work was carried out by Nwachukwu Christian Ejike, in the department of Physics, Faculty of Physical Sciences, University of Benin, Benin City under the supervision of Prof. E. Aghemenloh.

…………………………… ……………………..

PROF. E. AGHEMENLOH **DATE**

(Project Supervisor)

………………………………. ……………………..

PROF. C. O. AIGBOGUN **DATE**

(Head Of Department)

……………………………… ……………………..

EXTERNAL EXAMINER **DATE**

DEDICATION

This project is dedicated to God Almighty who provided me with everything I needed to make this work possible; my life, health, and the help of others.

I also dedicate this work to my late Mom and Sister Chioma Nwachukwu who saw me start this degree but is no longer here to see its end. This is for you sister. I know you are in a beautiful place now.

Lastly I dedicate this project to my Dad, brother and friends who supported me through this study and even funded it.

ACKNOWLEDGEMENT

I would like to sincerely thank my project supervisor Prof. E. Aghemenloh for his supervision even when I wasn’t giving my all to this work. And also for his guidance and support in providing ideas to get difficult-to-find research papers that I could use and learn from, as well as his fatherly advice and encouragement that kept me focused on finishing this work.

All thanks to my dad, Osita Nwachukwu, Mr. And Mrs Arighona, my brother Chimobi and friends for their support throughout the time I was working on this project

ABSTRACT

The surface free energy of nanoparticles is important as it gives us vital information about the reactivity and stability of nanoparticles.

Starting from a previously reported equation, a theoretical model that involves a specific term for calculating the cohesive energy of nanoparticles, is established in a view to describe the surface free energy of metallic nanoparticles (using different shapes of particle; sphere, cube and disk). The results show that the behaviour of surface free energy for spherical nanoparticles is the most realistic shape compared to disk and cubic shaped nanoparticles. As the surface free energy differs from shape to shape we also see that its value falls as the number of atoms (nanoparticle size) decreases. The results are in close agreement with the results of Fathi and Ayyad (2014).

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CHAPTER ONE

INTRODUCTION

1.1 HISTORY OF METALLIC NANOPARTICLES

The history of metallic nanoparticles dates back remarkably far - even though ancient civilizations didn't understand the science, they were using metallic nanoparticles as early as the 4th century CE. The famous Lycurgus Cup from Roman times contains gold and silver nanoparticles that give it unique optical properties, changing color when light shines through it.

However, the modern scientific understanding of metallic nanoparticles really emerged in the mid-19th century. Michael Faraday's work in 1857 with gold nanoparticles was groundbreaking - he created a stable gold colloid and began to understand how these tiny particles interacted with light differently than bulk gold.

The real explosion in metallic nanoparticle research came in the late 20th century, particularly the 1980s-1990s, when advanced microscopy techniques allowed scientists to actually visualize and manipulate matter at the nanoscale. This coincided with the emergence of nanotechnology as a distinct field.

As a result of their size and shape dependent physical, chemical and magnetic properties is of great interest with unusual optical, chemical and photoelectro-chemical and electronic properties.

1.2 SURFACE FREE ENERGY

Surface free energy is the excess energy present at the surface of a material compared to its bulk counterpart. It arises due to unsaturated atomic bonds at the surface, leading to a higher energy state. In nanoparticles, where the surface-to-volume ratio is significantly large, surface free energy influences several key properties like the thermodynamic stability, wetting and adhesion, Reactivity and catalysis.

Alkali metals (e.g., Li, Na, K, Rb, Cs) are characterized by their low ionization energies and high chemical reactivity. Due to their weak metallic bonding and large atomic radii, alkali metal nanoparticles exhibit relatively low surface free energies compared to transition metals. However, their high reactivity makes them prone to oxidation and instability in ambient conditions.

While, Transition metals (e.g., Fe, Co, Ni, Cu, Ag, Au, Pt, Pd) possess partially filled d-orbitals, leading to strong metallic bonding and high surface free energies. This results in enhanced catalytic properties and mechanical stability

The surface tension of metallic nanoparticles depends on the particle size and is different from those of the corresponding bulk metals.

1.3 COHESIVE ENERGY

The cohesive energy which is regarded as the energy required to separate the metallic crystal into individual atoms by destroying the metallic bonds. An already developed equation is used to account for the size effect on the surface free energy.

1.4 AIM AND OBJECTIVES

AIM

The aim of this work is to determine the surface free energy of spherical disk and cubic shaped metallic nanoparticles.

OBJECTIVES

The objectives of this work are to:

- Calculate the surface free energy of metallic nanoparticles
- Observe the changes of the surface free energy of nanoparticles with the number of atoms.

CHAPTER TWO

LITERATURE REVIEW

It was reported by Tolman (1949), Xiong ,Qi, Cheng and Wang (2011) that the surface energy should decrease with decreasing particle size, while others predicted an increase of the surface energy with decreasing size. The effect of size on the surface energy is important when the size is comparable with that of an atom.

Nanometallic particle such as copper and gold exhibit surface energies that a similar then that of the corresponding bulk materials, where as silver nanoparticles showed surface energy that is either close or greater than the bulk Berry (1952) and Wasserman and Vermaak (1970).

Alymov and Shorshorov (1999) suggest the surface tension of metallic nanoparticles depends on the particle size; the surface energies are different from those of their corresponding bulk metal.

The cohesive energy, which is the energy required to separate the metallic crystal into individual atoms by destroying the metallic bonds, an equation is developed to account for the size effect on the surface free energy of various metallic nanoparticles. The behaviour of surface energy with the number of atoms is investigated. The topic is interesting because the theoretical model with reasonable predictive quality for this subject is not readily available. The novelty in the present theoretical model is that the surface free energy of nanoparticles can be related to the heat of sublimation.

The model is based on some simplified assumption to calculate the surface free energy of metallic nanoparticles. We will most likely have errors associated with our results, but our results are in close agreement with the values obtained by Ahmed and Ayyad (2014).

CHAPTER THREE

THEORY AND METHODOLOGY

3.1 DERIVATION OF THE SURFACE FREE ENERGY OF NANOPARTICLES

In bulk metals, the surface effect results from the difference between the surface metallic atoms and interior atoms. This surface effect might be neglected for a bulk material but cannot be ignored when dealing with metallic nanoparticles because the surface atoms are less stable due to their lower coordination number..

The surface free energy of metallic nanoparticles consists of its bulk and surface. When the particle size reaches nanoscale, the ratio of its surface to volume becomes very large and so the total surface free energy becomes large.

The cohesive energy of nanoparticles depends on its size and increases with increasing particle size. When the particle size is large enough, cohesive energy will approach the value of the corresponding bulk material.

The Surface free energy is given by the formula according to Aqra and Ayyad(2014) ;

$$= \quad ^{-1} [0.195\frac{Es}{N}] \tag{3.1}$$

$$= \frac{\sqrt{3}}{2}\left(\sqrt{2}\,\frac{Vs}{N}\right)^{2/3} \qquad (3.2)$$

where;

N= Avogadro's number (6.02 X 10^{23} atoms mol^{-1})

Es= sublimation Energy

Vs= Molar volume of solid

= Area occupied per atom (cm^2/atom)

= Surface free energy

Note that 0.195 is the semi empirical fitting parameter.

Equation (3.1) is the surface free energy of the bulk metal, to get the surface free energy of a nanoparticle assuming the particle is spherical in shape. To get this the sublimation energy of the bulk materials has to be replaced by that if the nanoparticles because of size effects.

Since all nanoparticles are made up of identical spherical atoms, these atoms are closely packed. Based on this the number of atoms, n_t in tha nano particle is defined as the volume ratio of the nanoparticles and the atom.

Moreso, the number of atoms depends on the interatomic distances and packing modes, which means a packing fraction parameter is taken into account.

From Ahmed and Ayyad (2014), the maximum packing fraction ( ) = 0.74 and surface packing fraction ( )= 0.9

Recall;

Number of atoms(n_t) = ($V_{particle} \div V_{atom}$) × ( ) (3.3a)

Also;

number of surface atoms (ns) = ($A_{particle} \div A_{atom}$) × ( ) (3.3b)

And n_i (number of interior atoms) = $n_t - n_s$ (3.3c)

From a series of calculations by Aqra and Ayyad (2014) we derived the expression ;

$$n_i = n_t - [\frac{\eta}{\rho^{2/3}} (nt)^{2/3}] \quad (3.4a)$$

$$n_s = \frac{\eta}{\rho^{2/3}} (n_t)^{2/3} \quad (3.4b)$$

The cohesive energy which is a simple multiplication of the number of bonds and the bond energy with the total number of atoms taking into account the double counting of the bonds.

If the number of bonds of the interior atoms is taken to be B and the bond energy is $E_{b,}$

The cohesive energy of metal is the sum of all the bond energy of the metal system. The cohesive energy of the bulk material same as the sublimation energy at Zero Kelvin is given by:

$$E_c = E_s = \frac{1}{2} B n_t E_b \quad (3.5)$$

We assume that at the surface, half of the bonds are broken, the number of bonds of a surface atom with an interior atom is ¼B. The cohesive energy of the nanoparticles ($E_{particle}$) is half the sum of the sublimation energy of the surface and that of the interior materials.

Therefore,

$$E_{particle} = \tfrac{1}{2}\left[\tfrac{1}{4}Bn_sE_b + B(n_t - n_s)\,E_b\right]. \quad (3.6)$$

$$= \tfrac{1}{2}BE_b\left[\tfrac{1}{4}n_s + (n_t - n_s)\right]. \quad (3.7)$$

Substituting equation 2.4b for n_s

We arrived at the equation for the cohesive energy of the nanoparticles being a function of the cohesive energy of the bulk material.

$$E_{particle} = \left[1 - \frac{3}{4}\,\frac{\eta}{\rho^{2/3}}\,(nt)^{-\frac{1}{3}}\right]E_c. \quad (3.8)$$

Equation 3.8 accounts for the size dependence of the cohesive energy of metallic nanoparticles. With increasing the particle size the cohesive energy approaches that of the corresponding bulk metal. Though temperature effect can affect this it's effect is generally negligible (very small) so it is ignored in this calculation.

Using eq. 3.8 we can then calculate the cohesive energies of metal nanoparticles. We then can use the calculated surface energies of these metals to compute the surface free energy of the nanoparticles. The surface energies used for this calculation have been calculated and the experimental values were used Qi and Wang (2002).

Since eq. 2.8 gives us the cohesive energy of the nanoparticles to get the surface free energy ($_{\text{particle}}$) we substitute eq. 3.8 into eq. 3.1,

therefore,

$$_{\text{particle}} = {}^{-1}\left[\, 0.195 \left[1 - \frac{3}{4}\, \frac{\eta}{\rho^{2/3}} (nt)^{-\frac{1}{3}} \right] \frac{Ec}{N} \,\right] \qquad (3.9)$$

More so, the cohesive energy of metallic nanoparticles can also be determined if the nanoparticles is in a disk form we have the cohesive energy in a disk form,

$$E_{\text{particle}} = \left[1 - \frac{9}{16} \frac{\eta}{\rho^{2/3}}\, (nt)^{-\frac{1}{3}} \right] Ec \qquad (3.10)$$

And the Surface free energy becomes;

$$_{\text{particle}} = {}^{-1}\left[\, 0.195\, \left[1 - \frac{9}{16} \frac{\eta}{\rho^{2/3}}\, (nt)^{-\frac{1}{3}} \right] \frac{Ec}{N} \,\right] \qquad (3.11)$$

In addition to Qi and Wang (2002) determined the cohesive energy of metallic nanoparticles on the basis of assuming the nanoparticles in an ideal cubic form, give below;

$$E_{\text{particle}} = [1 - \frac{9}{2}\,(nt)^{-\frac{1}{3}}]\,Ec \qquad (3.12)$$

$$_{\text{particle}} = {}^{-1}\,[\,0.195\;\; [1-\frac{9}{2}(nt)^{-\frac{1}{3}}]\frac{Ec}{N}\,] \qquad (3.13)$$

Using these equations we are going to calculate the surface free energy of Cu,Ag,Au,Pt, W,Ta, Mo, Pd, Li, Na, K, RB, C's when they assume different shapes- spherical, disk and cubic shaped.

3.2 CALCULATION OF THE SURFACE FREE ENERGY OF SPHERICAL, DISK AND CUBIC NANOPARTICLE

Using the equations 3.9, 3.11 and 3.13 which represent the surface free energy of spherical, disk and cubic shaped nanoparticles respectively. The following parameters will be needed to solve for the surface free energy of nanoparticles, these parameters include ; molar mass (g/mol), density (g/cm^3), molar volume (cm^3/mol), cohesive energy, E_c (kJ/mol), area occupied per atom (cm^2/atom).

The ratio of the molar mass to density gives us the molar volume of the metal;

$$Molar\ volume, Vs = \frac{molar\ mass}{Density} \tag{3.14}$$

The table1 shows us the molar mass and density of these metals and their calculated molar volumes.

From equation 3.2 the molar volume helps us find the area occupied per atom (φ) which has been calculated and inserted into table 2. The cohesive energy used were the experimental values of Qi and Wang (2002). The number of particles nt takes the values 5,10,30,50,70,110,130,200,500 the values of their surface free energy are tabulated in tables 3,4 and 5.

Table 1: shows the molar mass, density and molar volume of metallic particles which we use in the calculation of the surface free energy.

Metals	Molar mass(g/mol)	Density(g/mol)	Molar volume, Vs(cm^3/mol)
Au	196.97	19.3	10.206
Ag	107.8	10.49	10.28
Pt	195.08	21.45	9.09
Cu	63.55	8.94	7.1085
W	183.8	19.28	9.53
Ta	180.95	16.65	10.87
Mo	95.95	10.22	9.39
Pd	106.42	12.007	8.86
Li	6.94	0.534	12.996
Na	23.0	0.97	23.71
K	39.1	0.862	45.36
Rb	85.47	1.534	55.72
Cs	132.9	1.89	70.3

Table 2: shows the values of the area occupied per atom used in determination of the surface free energy

metals	φ(x10^{-16} cm^2/atom)	φ^{-1}(x10^{16} cm^{-2}atom)
Au	7.199	0.1389
Ag	7.235	0.1382
Pt	6.665	0.1500
Cu	5.657	0.1768
W	6.877	0.145
Ta	7.503	0.133
Mo	6.82	0.1466
Pd	6.55	0.1526
Li	8.46	0.118
Na	12.63	0.079
K	19.46	0.051
Rb	22.3	0.045
Cs	26.1	0.038

To calculate the surface free energy of spherical gold particle when n_t=5

Using equation 3.9

$${}_{\text{particle}} = {}^{-1}\ [\ 0.195\ \ [1-\frac{3}{4}\frac{\eta}{\rho^{2/3}}(nt)^{-\frac{1}{3}}]\frac{Ec}{N}\ ]$$

for Au, ${}^{-1}$= 0.1389 x 10^{16} , Ec = 368kJ/mol

$${}_{\text{particle}} = 0.1389 \text{ x } 10^{16}\left[0.195\left(1-(0.75)(\frac{0.9}{0.818})(0.5848)368\right)\right] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195(1-(0.75)(1.1002)(0.5848)368)] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195(1-0.4826)368)] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195(0.5174)368)] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [37.1286] \div 6.02\times10^{23}$$

$$=0.1389 \text{ x } 10^{16} \times 6.02\times10^{-23}$$

$$= 0.859 \times 10^{16} \times10^{-23}$$

The multiple 10^3 come into play as we convert E_c in KJ/mol to J/mol, and 10^4 come in as we convert the unit of ${}^{-1}$(atom/cm^2) into atom/m^2

$${}_{\text{particle}}= 0.859 \times 10^{16} \times10^{-23} \times 10^3 \times10^4$$

$${}_{\text{particle}}= 0.859 \text{ J/mol}$$

$${}_{\text{particle}}= 0.859\text{mJ/mol}$$

To calculate the surface free energy of Disk shaped gold particle when n_t=5

From equation 3.11,

$$_{\text{particle}} = {}^{-1}\,[\,0.195\ \ [1-\frac{9}{16}\frac{\eta}{\rho^{2/3}}\,(nt)^{-\frac{1}{3}}\,]\ \frac{Ec}{N}]$$

for Au, $^{-1}$= 0.1389 x 10^{16} , Ec = 368kJ/mol

$$= 0.1389 \text{ x } 10^{16}\left[0.195\left(1-(0.5625)(\frac{0.9}{0.818})(0.5848)368\right)\right] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195(1-0.3619)368] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195(0.6381)368] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16}\ [0.195\times 234.8208] \div 6.02\times10^{23}$$

$$= 0.1389 \text{ x } 10^{16} \times 7.6063 \times10^{-23} \times 10^{3} \times10^{4}$$

Note : 10^3 was introduced from converting KJ/mol

10^4 was introduced from converting unit of $^{-1}$(atom/cm^2) into atom/m^2

= 0.993 J/mol

$_{\text{particle}}$ = 993 mJ/m^2

To calculate the surface free energy of Cubic gold particle when nt=5

From equation 3.13,

$$_{\text{particle}} = {}^{-1}\left[\ 0.195\ \left[1-\frac{9}{2}(nt)^{-\frac{1}{3}}\right]\frac{Ec}{N}\right]$$

for Au,

${}^{-1}$= 0.1389 x 10^{16} , Ec = 368kJ/mol

$_{\text{particle}} = {}^{-1}$ [0.195 [1-$\frac{9}{2}$(5)$^{-1/3}$]E$_c$ /N]

= 0.1389 x 10^{16} [$0.195(1-(4.5)(0.5848))368$)] ÷ 6.02×10^{23}

= 0.1389 x 10^{16} [$0.195(1-2.6316)368$)] ÷ 6.02×10^{23}

= 0.1389 x 10^{16} [$0.195(-1.6316)368$)] ÷ 6.02×10^{23}

= 0.1389 x 10^{16} [-117.08] ÷ 6.02×10^{23}

= 0.1389 x 10^{16} × -19.44 ×10^{-23}

= $-2.353\times10^{16}\times10^{-23}\times10^{3}\times10^{4}$

$_{\text{particle}}$ = -2.353 J/m^2

$_{\text{particle}}$ = -2353 mJ/m^2

The values of the surface free energy has been calculated following the process used above for spherical, disk and cubic shaped nanoparticles as the size of the nanoparticles changes and the results were summarised in tables below.

CHAPTER FOUR

RESULTS AND DISCUSSION

The surface free energy of gold, silver, platinum, copper, tungsten, tantalum, molybdenum,palladium,Lithium, sodium, potassium, rubidium and caesium was calculated for a spherical nanoparticles - values are obtained are tabulated in table 3.

Also, for a disk shaped nanoparticle the surface free energy is tabulated in table 4, while those of cubic- shaped which appear unrealistic in the nanoscale are also documented in table 5.

The number of atoms (n_t) were tabulated against the surface free energy, with values 5,10,30,50,70,90,110,130. The values of nt were also extended to 200 and 500.

Table 3: calculated surface free energy of spherical metallic nanoparticles of various sizes.

nt	5	10	30	50	70	90	110	130
metals								
Au	859	1017	1216	1283	1324	1349	1370	1656
Ag	614	784	934	986	1017	1037	1052	1272
Pt	1421	1691	2013	2126	2192	2233	2267	2740
Cu	998	1182	1414	1491	1539	1568	1592	1925
W	2093	2479	2964	3126	3226	3288	3338	4036
Ta	1747	2069	2475	2611	2694	2746	2787	3369
Mo	1621	1920	2295	2421	2498	2547	2585	3125
Pd	964	1142	1365	1440	1486	1515	1538	1859
Li	313	371	444	468	483	492	499	604
Na	142	168	201	212	219	223	227	274
K	77	91	109	115	119	121	123	149
Rb	59	74	88	93	96	98	99	119
Cs	50	59	70	74	76	78	79	96

Table 4: calculated surface free energy of disk-shaped metallic nanoparticles of various sizes.

nt	5	10	30	50	70	90	110	200	500
metals									
Au	993	1109	1246	1294	1322	1341	1355	1391	1434
Ag	811	906	1018	1058	1080	1096	1107	1137	1172
Pt	1749	1953	2195	2280	2329	2362	2386	2450	2527
Cu	1228	1371	1541	1601	1635	1659	1676	1721	1774
W	2574	2876	3231	3357	3429	3477	3514	3608	3720
Ta	2150	2401	2698	2803	2863	2904	2934	3013	3016
Mo	1904	2126	2389	2482	2536	2572	2598	2669	2751
Pd	1186	1325	1488	1546	1580	1602	1619	1662	1714
Li	385	430	484	502	513	521	526	540	557
Na	172	192	216	224	229	232	235	241	248
K	95	106	119	124	127	128	130	133	137
Rb	76	85	96	99	102	103	104	107	111
Cs	61	68	77	80	81	82	83	85	88

Table 5: calculated surface free energy of cubic-shaped metallic nanoparticles of various sizes.

nt	5	10	30	50	70	90	110	200	500
metals									
Au	-2353	-1570	-647	-320	-136	-6	88	333	625
Ag	-2074	-1384	-570	-282	-117	-5	77	293	551
Pt	-4471	-2984	-1228	-607	-252	-11	167	632	1187
Cu	-3140	-2095	-863	-426	-177	-8	117	444	833
W	-6583	-4393	-1808	-894	-371	-17	245	930	1747
Ta	-5497	-3668	-1510	-746	-310	-14	205	777	1459
Mo	-3919	-2615	-1077	-532	-221	-10	146	554	1040
Pd	-3033	-2024	-833	-412	-171	-8	113	428	805
Li	-985	-658	-271	-134	-56	-3	37	139	262
Na	-322	-215	-88	-44	-18	-1	12	46	85
K	-243	-162	-67	-33	-14	-1	9	34	64
Rb	-196	-130	-54	-27	-11	-1	7	28	52
Cs	-156	-104	-43	-21	-9	0	6	22	41

The surface free energy was plotted against the logarithm value of the number of atoms n_t(log n_t). fig 1 shows the graph of the surface free energy of alkali nanoparticles with respect to the size of the atoms. Fig 2, fig 3 and fig 4 is the graph of the size dependent surface free energy of gold, sodium and molybdenum respectively- their spherical, disk and cubic shaped nanoparticles taken into consideration.

Fig 1: Size dependent surface free energy of alkali metallic nanoparticles

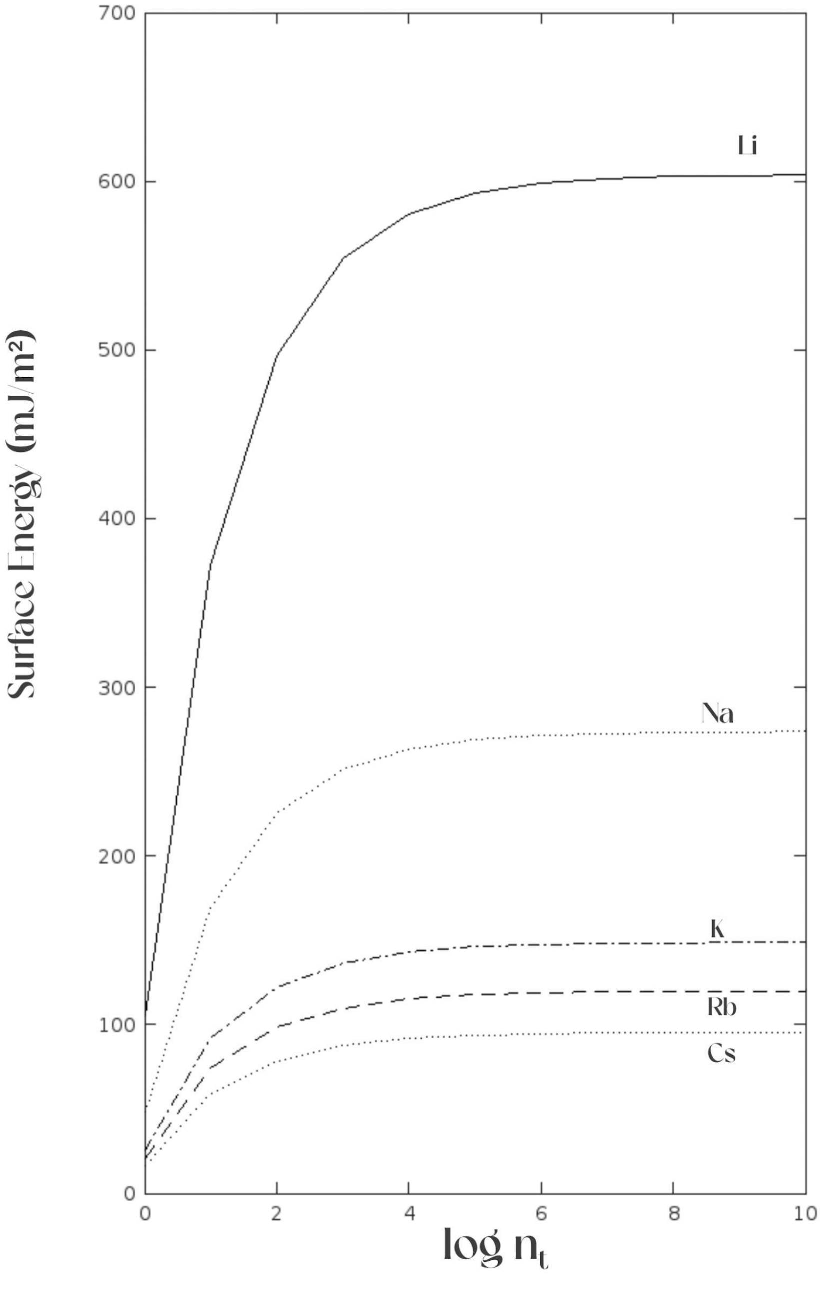


Fig 2: Size dependent surface free energy of spherical, cubic and disk nanoparticles of Gold(Au)

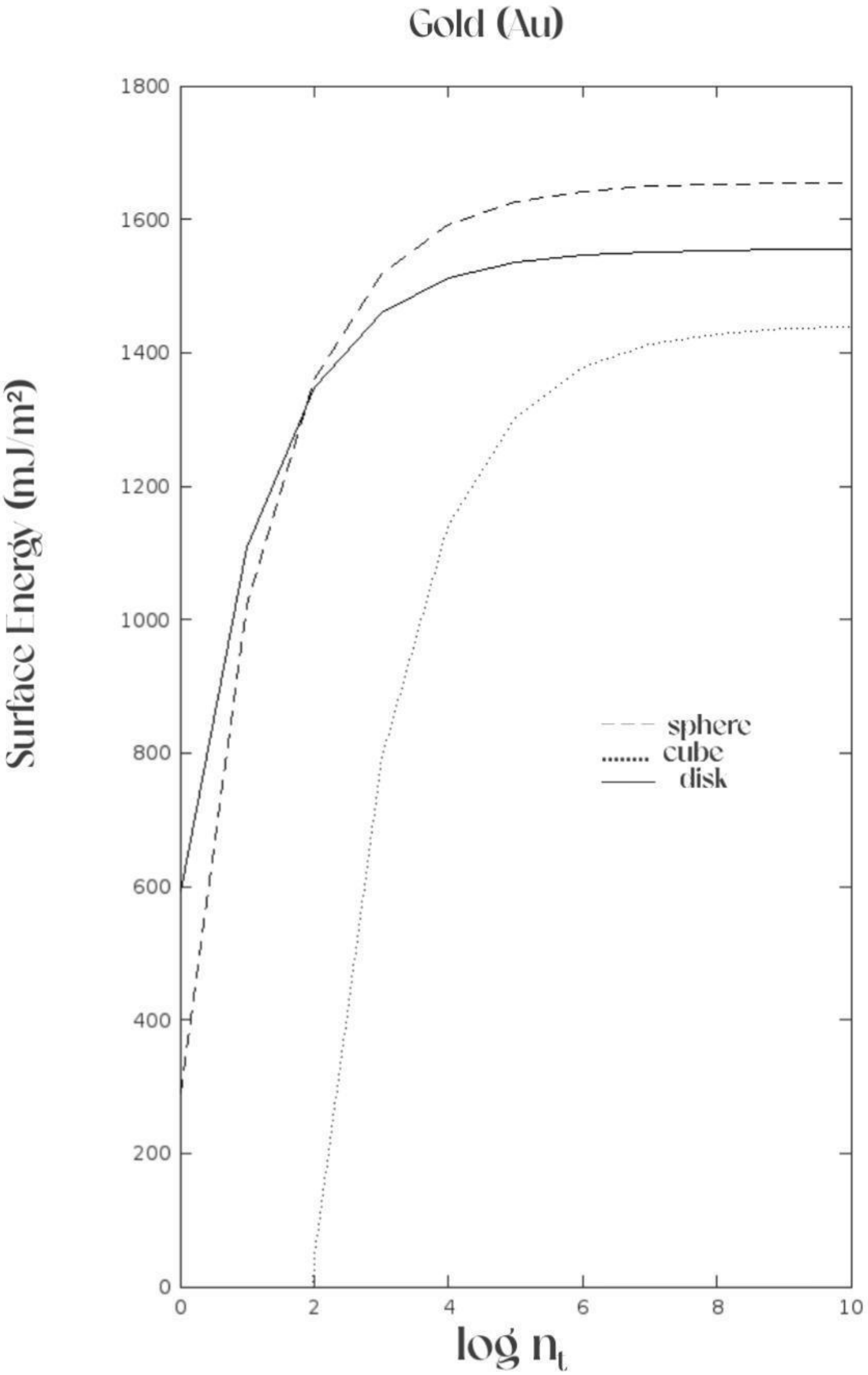


Fig 3: Size dependent surface free energy of spherical, cubic and disk nanoparticles of sodium(Na)

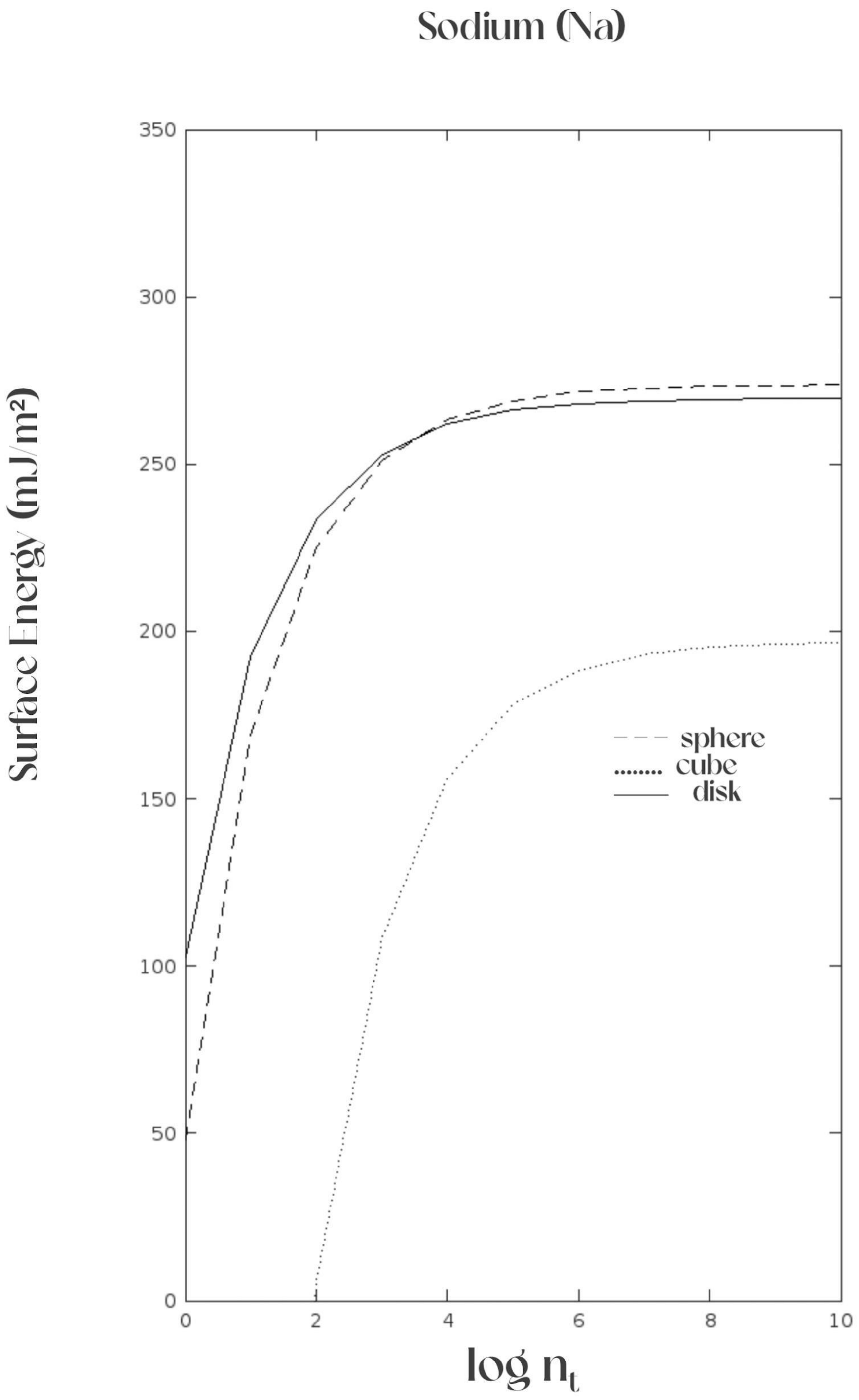
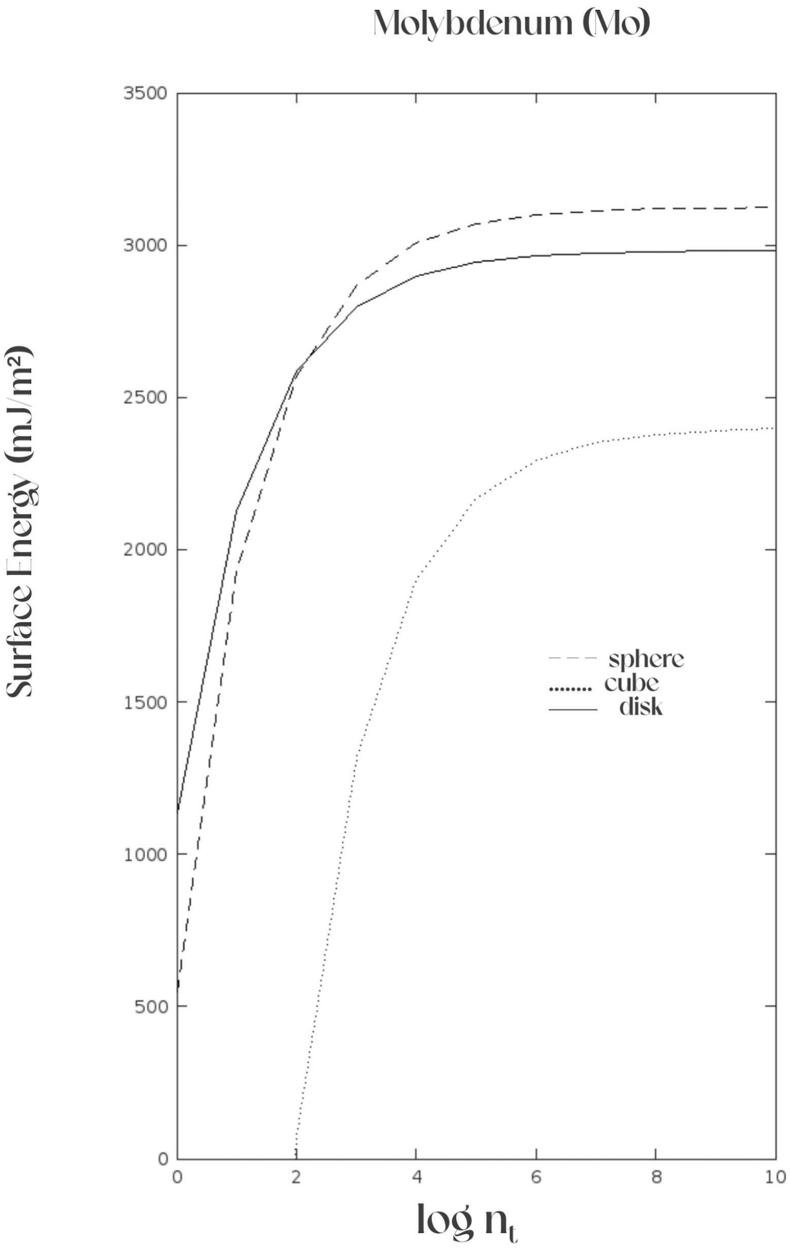

Sodium (Na)
Surface Energy (mJ/m²)
log n_t
350
300
250
200
150
100
50
0
0
2
4
6
8
10
sphere
cube
disk

Fig 4: Size dependent surface free energy of spherical, cubic and disk nanoparticles of Molybdenum (Mo)



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CHAPTER FIVE

FINDINGS, CONTRIBUTION TO KNOWLEDGE, CONCLUSION AND SUGGESTION FOR FURTHER STUDIES

5.1 FINDINGS

From our calculations and results obtained we discover that the surface energy reduces as the particle size decreases. The surface energy falls down very fast when the number of atoms reaches 110 atoms.

When the number of atoms is large, surface energy of the metal is obtained(bulk metal) and when it reaches the scale of a nanoparticle (less than or equal to 110 atoms) the surface free energy reduces to about 16% of the corresponding bulk value(table 3).

However the surface free energy decreases by 48% moving from its bulk value to 5atoms for a spherical nanoparticle and about 28% for a disk shaped nanoparticle. Thus we see by decreasing the particle size the surface energy also decreases.

From eq. 2.13 and table 5 the surface free energy of a cubic shaped nanoparticle as the nt moves from 100 and below goes to 0 and negative numbers. Thus the results of the surface free energy at these values of 0 is termed to be unrealistic when in comparison with the spherical particle that only goes to zero when the number of atoms is zero- which is in accordance with physical reality. The surface energy of this cubic shaped particle becomes realistic as the bulk form is attained. This indicates that nanoparticles are more realistic for the assumed spherical shape as compared to disk and cubic shaped particles.

5.2 CONTRIBUTION TO KNOWLEDGE

We have been able to determine the surface free energy of Cu, Ag, Au, PT, Mo,W, Ta, Pd and alkali metallic nanoparticles and we observe that the surface free energy decreases with decreasing metallic particle size.

5.3 CONCLUSIONS

From our graphs we notice the changes of the surface free energy as the logarithmic value of nt is used- the surface free energy always reduces with decreasing particle size.

The results of the calculated surface free energy value based on the presented model by Fathi and Ayyad(2014) is in comparison with the results they obtained. The proposed model clearly shows that the surface free energy decreases with decreasing material size and the calculated surface energies seems reasonable since at zero size the surface energy goes to zero and at relatively large size it approaches that of the bulk material.

The shape and structure of nanoparticles are strong functions of size. Due to the effect of the surface energy on the total cohesive energy, they are assumed to have spherical shape although they may be in different structures.

5.4 SUGGESTION FOR FURTHER STUDIES

In this work we have determined the surface tension of various metals and we have seen the changes in the surface free energy with the number of particles. Further studies should be made to determine the surface free energy of alloys and the effect of temperature and number of atoms in these alloys.

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