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Submitted by :

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THEME

surface tension of liquid alloys[Fe-Ni,Cu-Ni,Al-Ni,Fe-Cu]

Supported publicly before the jury composed of :

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Dedication

First and Foremost praise is to ALLAH, the Almighty, who gave me the strength and the life to accomplish my studies.

I dedicate this little work:

To my dear parents:

My father : Herzallah, My mother: Haniya.

To sacrifice their life for my success, I hope with all my heart that on this day you are proud of me, and that I realize one of your dreams. Great God gives you good health; long life and happiness Amine

My beloved brothers and sisters : *Zeinab, Mohammed Amin, Osama, Ahmad, Abdulrezak, Hagar.*
May God protect you and grant you a bright future with a life full of joy, happiness and success.

To My dearest fiance : *Omar Oulad laid*
Who leads me through the valley of darkness with light of hope and support.

To my dear best friends : *Asia zebda, hoda mekky.*

Whom have always been a source of support and encouragement during the challenges of my entire university life

To all my family, the symbol of love and giving

To all my friends and classmates

Mebarka Bettache

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For all those whom I have forgotten, here they express my sincere gratitude and forgive my forgetfulness .

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Table of Glossary of Notations and Symbols

notation	**designations**	**Unit**
W	The work	***J/mol***
A	The area	$\boldsymbol{m^2}$
σ	Surface tension	$\boldsymbol{J/m^2}$
P	Pressure	***atm***
U	The internal energy	***J***
Q	The heat	***J/mol***
T	The temperature	***°K***
S	The entropy	***J/°K***
H	The enthalpy	***J***
G	The Gibbs energy	***J***
F	The free energy	***J***
B_0	Bond number	$\boldsymbol{Kg.m}$ $/(\boldsymbol{N.s}\text{^}\boldsymbol{2})$
V	The volume	$\boldsymbol{m^3}$
P	The density	***Kg/*** $\boldsymbol{m^3}$
$\boldsymbol{a_i^l}$	Thermodynamic activity	/
$\boldsymbol{\mu_\nu^l}$	Chemical potential of Component	***J/mol***
$\boldsymbol{\mu_\nu^{sl}}$	Chemical potential of $\boldsymbol{\nu}$ Component at the surface	***J/mol***
θ	Contact angle	***the degree*** °
$\boldsymbol{\omega_\nu}$	Molar area of component	$\boldsymbol{m^2}$***/mol***
$\boldsymbol{\Omega}$	miscibility energy of component	***J/mol***
$\boldsymbol{\Omega^s}$	miscibility energy of Component at the surface	***J/mol***
$\boldsymbol{\sigma_{0\nu}}$	surface tension of pure meta	$\boldsymbol{J/m^2}$

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General Introduction

General Introduction

Surface phenomena have been attracting the attention of researchers for decades. The phenomena of adsorption, surface segregation and others have been the subject of much theoretical research in the last century [1-9]. Among the surface phenomena the surface tension took more attention.

Surface tension is one of the important surface properties of liquid alloys. It plays an important role to understand surface-related phenomena, such as interfacial adhesion and wettability between the soldering material and the substrate[5]. and it Used to interpret the results of a particular volume calculation and surface properties of materials. However, it should be noted that the fact seems somewhat interesting, because on the one hand, the size and surface varies by contribution Surface separation is absent in size for size, because the concentration of atoms on the surface differs from its concentration in size.

The present work deals with the equilibrium segregation of surface and surface tension of liquid alloy binary. It presents a simple theoretical model based on thermodynamic concepts and which makes it possible to calculate certain physicochemical surface and interface properties. An application is made on a set of binary metal systems.

This work is divided into two chapters. The first concerns the basic notions of surface tension and Explains different methods to measure surface tension.

In the second chapter, we propose a simple thermodynamic model that treats the segregation and calculate the surface tension

Our formulation is based on theoretical foundations of proven bases. We treat the equilibrium between the fraction of surface and volume fraction for systems

We finish our work with a general conclusion and perspective.

Chapter I

the surface tensions

I.1. Surface tension

Surface tension in the static liquid has a property that makes it behave as the elastic sheet and at surface the liquid caused by forces between the molecules, where a every molecule in the interior of a liquid be attracted to every other molecules because the polar properties or because of the ionic properties equally from all directions. The molecules near the surface are attracted by molecules to all directions except the above direction, which is an unbalanced force that pulls the molecule into the liquid, making the surface tend to shrink to take as little space as possible (figure I.1). Then this is the reason why the drops of a liquid in air are assumed to be spherical, because for a given volume the spherical shape has the smallest possible area.

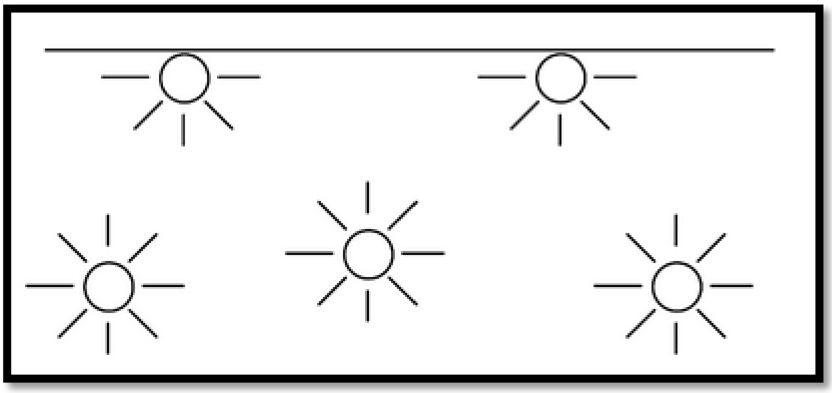

Fig.I.1: Surface tension is a result of the net inward pull on the surface molecule[10]

Surface tension is scientifically defined as the forces that perpendicularly to the unit of length from a point on the surface and is measured in units of Newton / meter. We can be defined equally as the energy required to increase the surface area by one square meter, that is, a tour per square meter (equivalent to $N.m^{-1}$) can be measured. The value of surface tension of liquid is dependent upon the nature of liquid itself as shown on table (I.1):

TABLE.I.1: surface tension for some liquids

Liquid	Temperature	Surface tension N/m
Water	293.15	0.0728[5]
Glycerine	293.15	0.0634[5]
Ethyl alcohol	293.15	0.0227[5]
Copper	1357	1.339[11]
Gold	1338	1.162[11]
Silver	1234	0.914[11]

The surface tension is responsible for the formation of liquid droplets, soap bubbles, and textiles, as well as the rise of liquids in the capillary tube (capillaries), the absorption of liquids by porous substances , and the ability of liquids to wet the surface[12].

I.2.Surface tension and surface energy

The idea of a tension in the free surface of a liquid is familiar as an explanation of the tendency of a liquid surface to assume the form having a minimum area, as shown in the shape of a bubble or a drop of liquid[13]. We found that to increase the surface area of a liquid (i.e stretch a soap film on a wire frame), it is necessary to apply a large force to move some of the molecules from the soles of the liquid to the surface (Figure.I.2). The magnitude of this force can be obtained by consideration of the energy change involved in an infinitesimal movement of the cross-bar by a distance dx, which can be achieved by doing reversible work on the system, thus raising its free energy by a small amount Fdx. If the system is at equilibrium, this change in (free) energy δW must be exactly equal to the increase in surface (free) energy associated with increasing the area of both surfaces up and down of the soap film ($2\ l\ dx$). Hence, at equilibrium[10] :

$$\delta W = Fdx = 2\ \sigma\ l\ dx \tag{I.1}$$

Thus, the surface energy of the liquid called also surface tension can be expressed by:

$$\sigma = {}^{F}/_{2l} \tag{I.2}$$

The dimensions of surface energy σ is N/m (equation I.2) or J/m^2 (equation I.1).

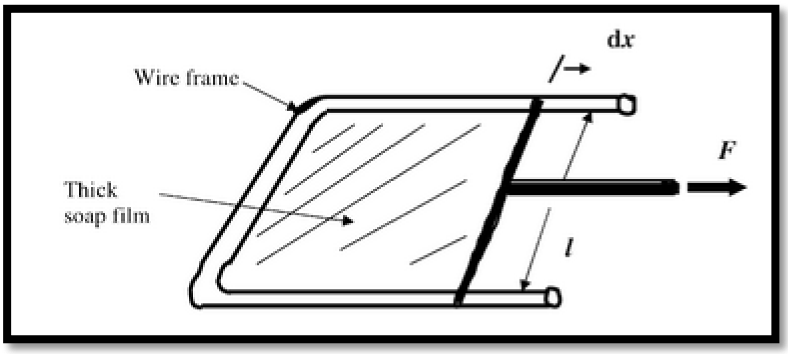

Fig.I.2: Diagram of a soap film stretched on a wire frame[10] .

I.3.Surface Tension as Mechanical Quantity

I.3.1. Laplace’s law (Influence of the curvature of a surface)

With the definition of γ as a free energy per unit surface, we can think of the surface tension as a tensile force of an interface, opposing any deformations leading to an increase in the surface area. If we deform the liquid such that its surface A increases by an amount dA, the work performed is $dW = \gamma dA$. If no force acts normal to a tensioned surface, the surface must remain flat. But if the pressure on one side of the surface differs from on the other side, the pressure difference times the surface area results in a normal force[14].

Consider an element dS of a curved interface with radii of primary curvatures (in two orthogonal directions) R_1 and R_2 (see Figure I.3.). Each boundary line of that element is subject to forces of surface tension exerted by the rest of the interface[15].

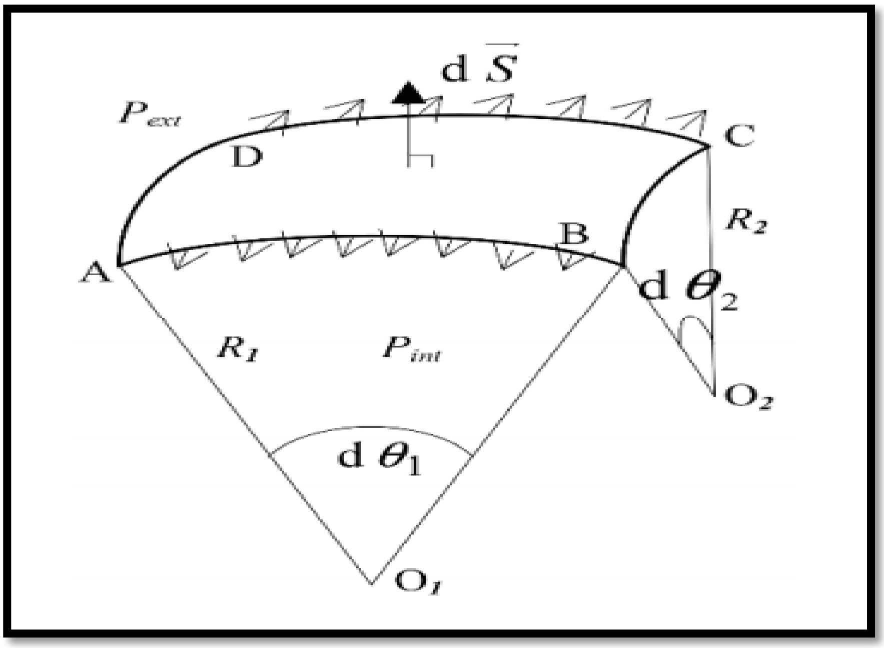

Fig.I.3: *Radii of curvature of a curved surface[15].*

At mechanical equilibrium, the resultant of these forces is canceled out by the forces exerted on the surface by the pressure P_{int} inside the curve and P_{ext} outside of it. As the tangential components, two by two, cancel one another out, it is easy to calculate the normal components. Thus, for instance, on the side AB, the force experienced by the surface element is[15]:

$$-R_1 d\theta_1 \sigma \sin\frac{d\theta_2}{2} \approx -\frac{1}{2} R_1 d\theta_1 \sigma d\theta_2 \qquad (I.3)$$

Since sin $d\theta_1$ is small,

$$(\gamma R_1 d\theta_1)\sin d\theta_2 \approx (\gamma R_1 d\theta_1).d\theta_2 \qquad \text{(I.4)}$$

The projection of the resultant of all the components, which takes the value of 0, is written:

$$-\sigma R_1 d\theta_1 d\theta_2 - \sigma R_2 d\theta_2 d\theta_1 + (P_{int} - P_{ext}) R_1 d\theta_1 R_2 d\theta_2 = 0 \qquad \text{(I.5)}$$

From this, we deduce:

$$P_{int} - P_{ext} = \sigma\left(\frac{1}{R_1} + \frac{1}{R_2}\right) \qquad \text{(I.6)}$$

This is Laplace's law, which gives the expression of the discontinuity in pressure on either side of a curved interface as a function of the surface tension and of the primary radii of curvature of that curved surface[15].

This is the fundamental equation which describes the equilibrium shape of menisci such as drops and bubbles. Analysis of equation (I.6) shows that :

1. where the meniscus is spherical, i.e. . $R_1 = R_2 = r$; therefore

$$\Delta p = 2\sigma / r \qquad \text{(I.7)}$$

2. For a cylindrical surface, $R_1 \rightarrow \infty$; therefore

$$\Delta p = \sigma / R_2 \qquad \text{(I.8)}$$

3. And when the surface is planar, i.e. $R_1 = R_2 = \infty$; therefore

$$\Delta p = 0 \qquad \text{(I.9)}$$

It is also possible for a portion of a surface to be locally saddle shaped; in such a case the two radii of curvature lie on opposite sides of the surface and have different signs. It is possible for p to be zero in this situation also[13].

I.3.2. Capillary action

Capillary action is the elevation or depression of the surface of a liquid where it is in contact with a solid, such as the sides of a tube. This phenomenon is an exception to the hydrostatic law that a liquid seeks its own level. It is most marked in capillary tubes, ie, tubes of very small diameter. Capillary action depends on the forces created by surface tension and by wetting of the sides of the tube. If the forces of adhesion of the liquid to the solid (wetting) exceed the forces of cohesion within the liquid (surface tension), the liquid will rise up the tube, that is, it will rise above the hydrostatic level. If the forces of cohesion exceed the forces of adhesion, the liquid will be repelled from the sides of the tube, that is, it will fall below the hydrostatic level[16]. as shown in Figure (I.4).

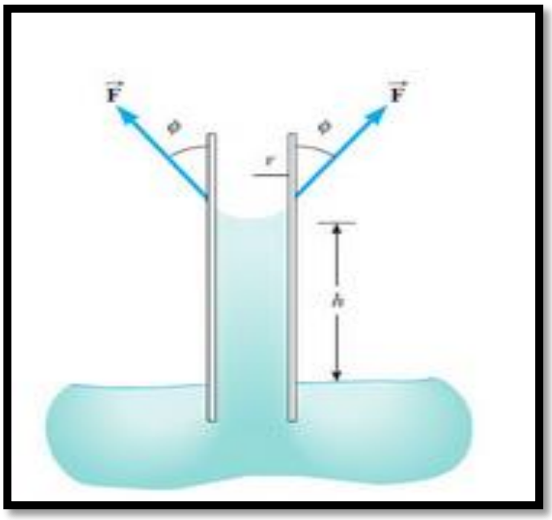

Fig.I.4: Capillarity phenomena: concave meniscus[17]

In rising of liquid, at the point of contact between liquid and solid, the upward force of surface tension is directed as shown in the figure[17]. From Equation (I.10), the magnitude of this force is

$$F = \gamma L = \sigma(2\pi r) \qquad \text{(I.10)}$$

The vertical component of this force due to surface tension is

$$F_v = \sigma(2\pi r)(\cos\theta\ ) \qquad \text{(I.11)}$$

where is the angle formed by the tangent of meniscus at the contact with the tube and the vertical axis.

In equilibrium the upward force is equal to the weight of liquid. If Mg is weight of this liquid, this weight is:

$$Mg = pVg = \rho g \pi r^2\, h \qquad \text{(I.12)}$$

where ρ is the density of the liquid and V its volume.

Applying Newton's second law for equilibrium the force F_v in equation (I.11) is equal to Mg in equation (I.12), we obtain:

$$\sigma(2\pi r)(\cos\theta\ ) = pg\pi r^2\, h \tag{I.13}$$

Solving for h gives the height to which liquid is drawn into the tube :

$$h = \frac{2\gamma}{\rho g r}\cos\theta \qquad \text{(I..14)}$$

The above expression (1.14) shows that the height up to which a particular liquid rises in different capillary tubes of the same material depends upon the radius of the bore such that $r\,h\ =\ Const$. Thus liquid rises to a greater height in a narrow tube, and from the same expression also gives the height to which liquid goes down into the tube. If $\emptyset > 90°$, $\cos\emptyset$ is negative, liquid falls in a capillary tube[16].

If the forces of cohesion exceed the forces of adhesion, the surface of the liquid will be convex (example for Hg), and the liquid will be repelled from the sides of the tube, that is, it will fall below the hydrostatic level [18]as shown in Figure (I.5).

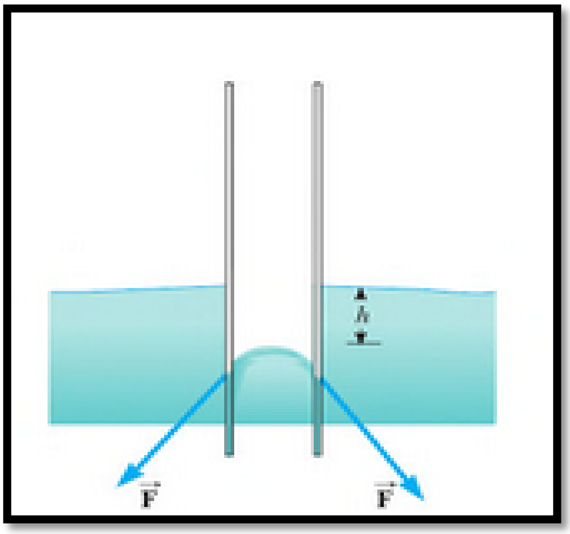

Fig.I.5: Capillarity phenomena: convexe meniscus[17]

I.3.3. Surface tension as thermodynamic quantities

The systems to be considered will consist of two bulk phases α (the liquid phase) and β (the vapor phase) and their mutual interface called the γ phase, and it will be supposed throughout that a, B and the interface are in equilibrium with each other[18].

For a closed system, neglecting surface effects for the moment, the differential expression for the internal energy U of the system is[18]:

$$dU = dQ + dW, \qquad \text{(I.15)}$$

where dQ is the heat taken up by the system for an infinitesimal change, and dW is the work done on the system. For a system at equilibrium, infinitesimal changes are reversible and, if the work done is associated entirely with volume changes, dW= PdV, where V is the volume and P the pressure of the system. Further, dQ=TdS where s is the entropy and T the temperature of the system. Equation (I.15) may therefore be written[18]:

$$dU = TdS - PdV \qquad \text{(I.16)}$$

The total volume of the system is the sum of those three volumes of α and β and γ phases:

$$\mathrm{V} = \mathrm{V}^{(\alpha)} + \mathrm{V}^{(\beta)} + \mathrm{V}^{(\gamma)} \qquad \text{(I.17)}$$

The same is true for the other extensive functions, which will all be the sum of three terms so The total internal energy of the system comprising α, β and interface is the sum of the internal energies of each of the phases, and so where $\mathrm{U}^{(\alpha)}$ and $\mathrm{U}^{(\beta)}$ and $\mathrm{U}^{(\gamma)}$ are the internal energies of α, β and the interface respectively[15].

$$\mathrm{U} = \mathrm{U}^{(\alpha)} + \mathrm{U}^{(\beta)} + \mathrm{U}^{(\gamma)} \qquad \text{(I.18)}$$

And the entropy:

$$\mathrm{S} = \mathrm{S}^{(\alpha)} + \mathrm{S}^{(\beta)} + \mathrm{S}^{(\gamma)} \qquad \text{(I.19)}$$

And the quantities of material:

$$\mathrm{n} = \mathrm{n}^{(\alpha)} + \mathrm{n}^{(\beta)} + \mathrm{n}^{(\gamma)} \qquad \text{(I..20)}$$

The extensive variables defining a mole of the system form the set ε_U, such that:

$$\varepsilon_U = \left\{\mathrm{S}^{(\alpha)}, \mathrm{S}^{(\beta)}, \mathrm{S}^{(\gamma)}, \mathrm{V}^{(\alpha)}, \mathrm{V}^{(\beta)}, A\right\} \qquad \text{(I.21)}$$

This set does not contain the volume of the layer $\mathrm{U}^{(\gamma)}$, because we assume this small and thin volume as an plan with an area equal to A. By expressing the variation of the internal energy, we obtain[15]:

$$dU = TdS^{(\alpha)} + TdS^{(\beta)} + TdS^{(\gamma)} - P^{(\alpha)}dV^{(\alpha)} - P^{(\beta)}dV^{(\beta)} + \sigma dA \qquad \text{(I.22)}$$

The surface energy (surface tension), which is the intensive value conjugate to the area, is defined as the partial differential of the internal energy in relation to the area[15]:

$$\sigma = (\partial U/\partial A)_{S,V^{(\alpha)},V^{(\beta)},n} \qquad \text{(I.23)}$$

If we now choose the set of variables ε_H, defined by:

$$\varepsilon_H = \{\mathrm{S}^{(\alpha)}, \mathrm{S}^{(\beta)}, \mathrm{S}^{(\gamma)}, \mathrm{P}^{(\alpha)}, \mathrm{P}^{(\beta)}, A\} \qquad \text{(I.24)}$$

the potential function would be the enthalpy, defined by:

$$\mathrm{H=U+PV} \qquad \text{(I.25)}$$

Thus, using relations (3.12) and (3.15), we find the differential of H is:

$$dH = TdS^{(\alpha)} + TdS^{(\beta)} + TdS^{(\gamma)} + V^{(\alpha)}dP^{(\alpha)} + V^{(\beta)}dP^{(\beta)} + \sigma dA \qquad \text{(I.26)}$$

and the surface energy would be such that:

$$\sigma = (\partial H/\partial A)_{S,P^{(\alpha)},P^{(\beta)},n} \qquad \text{(I.27)}$$

If we choose the set of variables ε_F defined by:

$$\varepsilon_F = \{T,, \mathrm{V}^{(\alpha)}, \mathrm{V}^{(\beta)}, A\} \qquad \text{(I.28)}$$

the potential function would be the free energy, defined by F :

$$\mathrm{F=U-TS} \qquad \text{(I.29)}$$

Hence, using relations (I.22) and (I.29), we can find the differential of F[15]:

$$dF = -S^{(\alpha)}dT - S^{(\beta)}dT - S^{(\gamma)}dT - P^{(\alpha)}dV^{(\alpha)} - P^{(\beta)}dV^{(\beta)} + \sigma dA \qquad \text{(I.30)}$$

and the surface energy would be such that:

$$\sigma = (\partial E/\partial A)_{T,V^{(\alpha)},V^{(\beta)},n} \qquad \text{(I.31)}$$

If we choose the set of variables ε_G, defined by:

$$\varepsilon_G = \{T,, \mathrm{P}^{(\alpha)}, \mathrm{P}^{(\beta)}, A\} \qquad \text{(I.32)}$$

the potential function would be the Gibbs energy, defined by:

$$\mathrm{G=H-TS} \qquad \text{(I.33)}$$

Thus, using relations (I.26) and (I.33), the differential of G would be[15]:

$$dG = -S^{(\alpha)}dT - S^{(\beta)}dT - S^{(\gamma)}dT + V^{(\alpha)}dP^{(\alpha)} + V^{(\beta)}dP^{(\beta)} + \sigma dA \qquad \text{(I.34)}$$

and the surface energy would be such that:

$$\sigma = (\partial G/\partial A)_{T,P^{(\alpha)},P^{(\beta)},n} \qquad (I.35)$$

I.4.Techniques of surface tension measurement

There a host of phenomena can be used to determine surface tension value. Consequently, very many methods of measuring σ have been described.

I.4.1. The sessile drop Technique

The sessile drop technique is drop shape method. A liquid drop is placed on a flat, unwetted, solid support (sessile drop: Fig. I.6.). Figure I.7 shows the equilibrium profile of a sessile drop of liquid at rest on a horizontal solid surface. At any point B on the surface contact, the principal radii of curvature are r_1 and r_2 and the excess pressure due to surface curvature is given by the Laplace equation[9]:

$$\sigma\left(\frac{1}{r_1}+\frac{1}{r_2}\right) = \rho g(h-z) + C \qquad (I.36)$$

where ρ is the density, g the gravitational acceleration, and h the height.

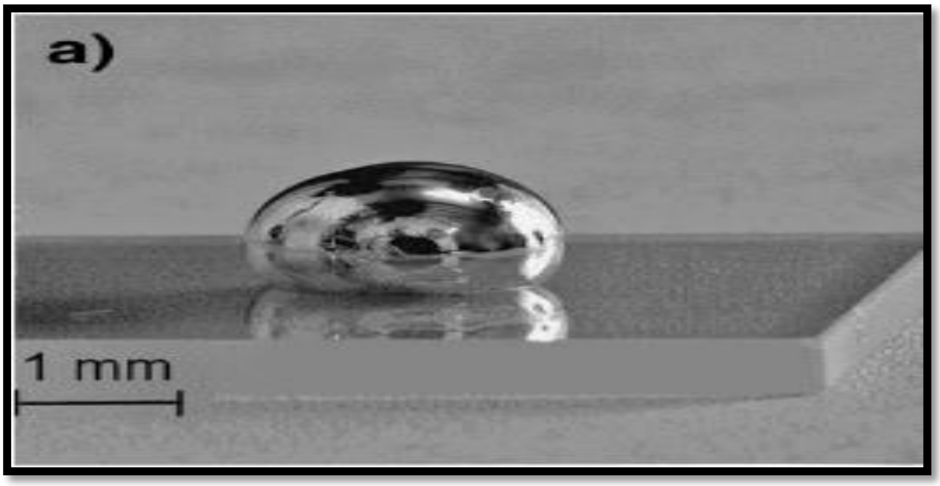

Fig.I.6: Picture of: sessile drop (Au on SiO2-single crystal) [9]

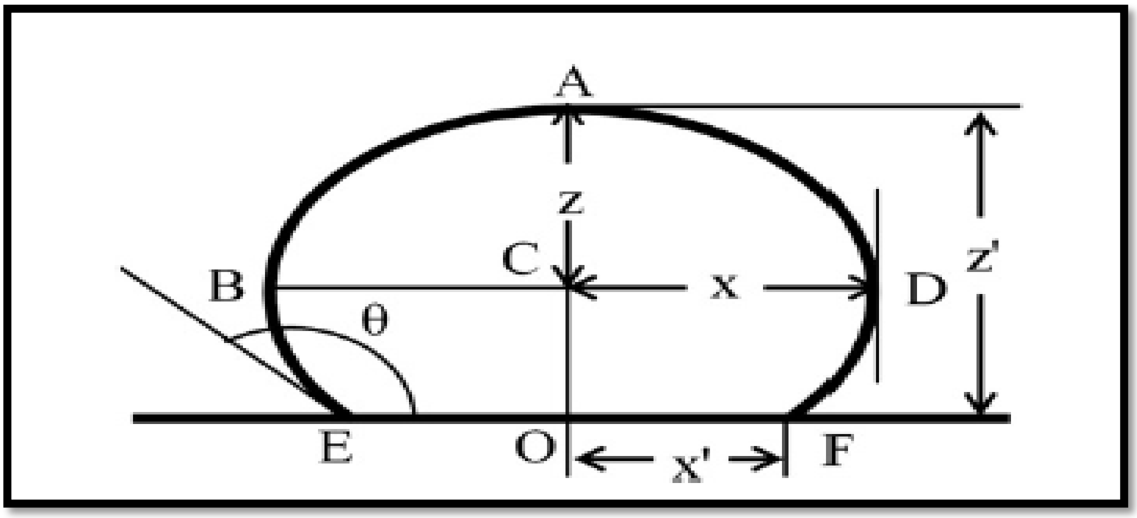

Fig .I. 7: Equilibrium profile coordinates of a sessile drop[9].

At the apex (z=h), the two radii of curvature are equal (r_1=r_2=b). Therefore, C=2 σ/b and:

$$r_2 = \frac{x}{\sin\theta} \qquad \text{(I.37)}$$

Hence, when equation (I.37) is substituted in equation (I.36), it may be arranged as follows[9]:

$$r_1 = \frac{1}{\frac{\rho g}{\sigma}.(h-z)+\frac{2}{b}-\frac{\sin\theta}{x}} \qquad \text{(I.38)}$$

Finally, the following equation is obtained:

$$\frac{(h-z)B_0}{b^2}+\frac{2-B_0}{b}-\frac{\sin\theta}{x}=0 \qquad \text{(I.39)}$$

where Bo is the Bond number defined as:

$$B_0 = \frac{\rho g b^2}{\sigma} \qquad \text{(I.40)}$$

B_0 is determinate by a geometric approach (equation 1.39), than σ is calculated via equation (I.40). Ideally, measurements should be made on the profiles of non-wetting sessile drops ($\theta >$ 90°), since though it is possible to determine σ from drops for which $\theta <$ 90°, the overall accuracy is reduced. Large sessile drops should be used for the best accuracy, but in practice, it is usually difficult to obtain large drops in isolation that are truly axisymmetric. To overcome problems of asymmetry, the 'large drop' method can be used. This modification of the sessile drop technique has two advantages in that it produces a large axisymmetric meniscus and can be used with both wetting and non-wetting system[4].

I.4.2. The pendant drop Technique

The pendant drop technique is drop shape method (figureI.8). This technique has several advantages: it is applicable to both free interfaces (air / liquid) and buried interfaces (liquid / liquid), it also allows in situ measurements and non-destructive[4]. The configuration of the pendent drop shape results from the balance between surface tension and gravitational forces acting in the system. A pendent drop is, in effect, an inverted sessile drop and is mathematically described by equation (1.36), where b=R_0. In the case of the pendent drop, the origin is taken to be at the bottom of the drop. Figure (I.9) specifies the definition of the coordinate system[8].

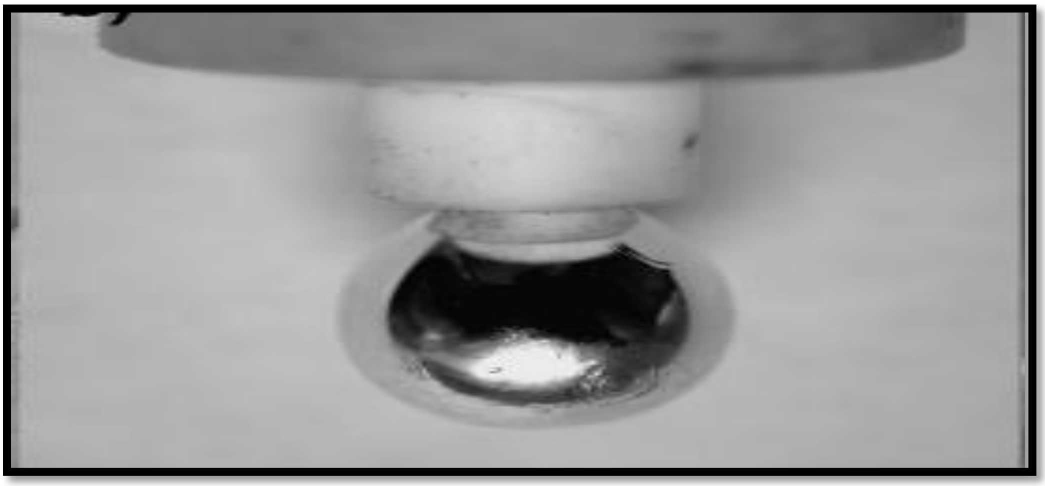

Fig.I.8: Picture of: pendant drop (Al from Al_2O_3-polycrystal capillary) [9].

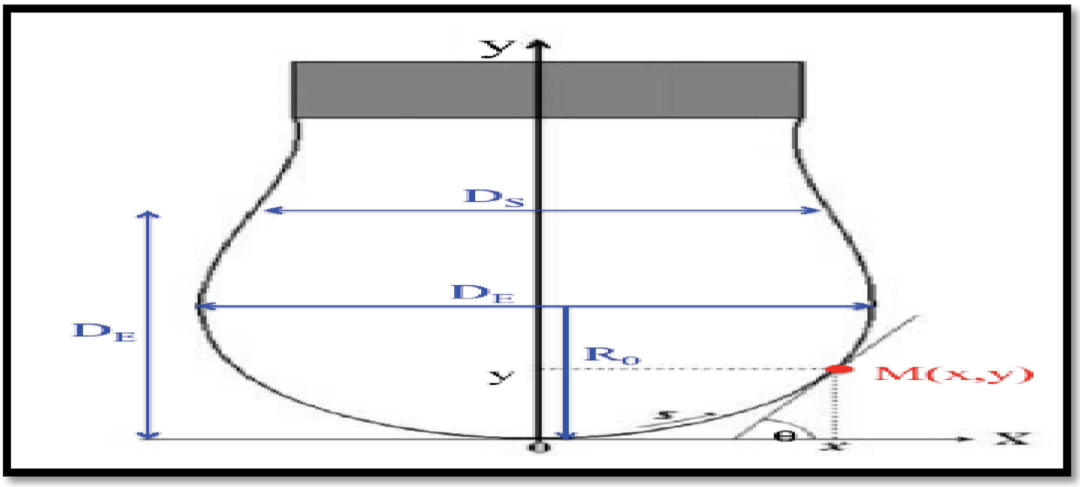

Fig. I.9: Notation used to describe the shape of a pendant drop[8].

To obtain a parametric equation of the drop profile, we will define the curvilinear abscissa s from the top O of the drop and the angle θ as shown in Figure (I.9). Using the X, Y and S dimensioned coordinates that $\mathrm{X} = \frac{\mathrm{x}}{\mathrm{R_0}}$, $\mathrm{Y} = \frac{\mathrm{y}}{\mathrm{R_0}}$, $\mathrm{S} = \frac{\mathrm{s}}{\mathrm{R_0}}$ and using $R_1 = \frac{ds}{d\theta} =$ and $R_2 = \frac{x}{\sin\theta}$, we can rewrite the Young-Laplace equation in parametric form next :

$$\frac{d\theta}{dS} = 2 \pm \beta Y - \frac{\sin\theta}{X} \qquad \text{(I.41)}$$

$$\frac{dX}{dS} = \cos\theta \qquad \text{(I.42)}$$

$$\frac{dY}{dS} = \sin\theta \qquad \text{(I.43)}$$

$$\beta = \frac{\Delta\rho g R_0^2}{\sigma} \qquad \text{(I.44)}$$

The positive sign + (respectively negative -) before b in equation (I.41) corresponds to a rising drop (respectively a hanging drop) formed according to the density of the two respective fluids.

As can be seen, equation (I.31) is a nonlinear parametric equation, which has no analytical solution in the general case. Historically, before the advent of computers capable of solving numerically this equation, it was proposed the use of tables that [1] allowed, from the form of drops pendent, to go back to the interfacial tension. These tables were built by calculating The report $\sigma = (\frac{D_E}{D_S})$, where DE is defined as the maximum diameter of the drop, and DS is the diameter of the drop at a distance DE from the top. The advent of numerical computations and the digitalization of images have led to the development of faster and more precise methods [3], based on an adjustment between the profile of a droplet and the numerical resolution of the Young- Laplace which allows to precisely find the values of the parameters β and $\mathrm{R_0}$.

I.4.3.Maximum bubble pressure (MBP) and maximum pressure in a drop (MPD)

Both these techniques can be considered as quasidynamic methods since new surfaces are being produced throughout the experiment. Figure (I.10) illustrates the principle behind a conventional MBP apparatus, in which a capillary tube of known radius r is immersed in the fluid to a known depth *h*. A gas/liquid meniscus is produced at the capillary tip by progressively increasing the gas pressure in the tube until the applied pressure is sufficient for the meniscus to form an independent bubble which detaches from the orifice. The maximum pressure at this point is recorded by a suitable transducer system and, from this value, the surface tension σ can be calculated. Considerably less attention has been paid to the MPD technique, which is similar in principle, except that the roles played by gas and fluid are interchanged, in that the pressure is applied to the fluid which is forced through a capillary into the gas phase[4].

If the capillary tube shown in figure (I.10) has a sufficiently small radius r, the meniscus produced at the orifice will have a spherical contour. As the pressure is increased, the spherical radius of the meniscus decreases and ultimately attains a minimum value when the profile is a hemisphere (radius = r). At this point the pressure on the meniscus is maximum and a bubble will be produced. In this case, the two principal radii of curvature are equal and following from the Laplace relation (equation I.45) the pressure P_σ in the bubble of detachment is given by[4]:

$$P_\sigma = 2\sigma/r \qquad \text{(I.45)}$$

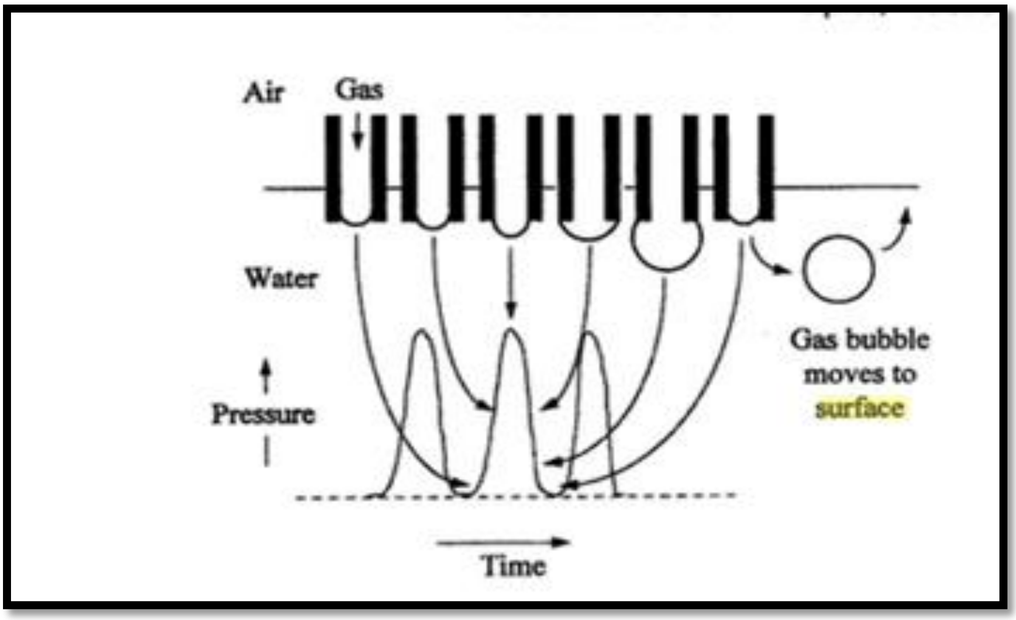

Fig.I.10: Maximum bubble pressure method of determining the surface tension of liquids[23].

If the tip of the capillary is immersed to a depth h in the fluid, then the total pressure P_{max} acting at the point of bubble detachment is given by[4]:

$$P_{max} = P_\sigma + \rho g h = \frac{2\sigma}{r} + \rho g h \qquad \text{(I.46)}$$

where ρ is the density difference between the fluid and gas and g the acceleration due to gravity.

In equation (I.46), P_{max} varies linearly with h and from a straight line plot, σ can be determined by extrapolation to the intercept on the P_{max} axis, at Which point $P_{max} = P_\sigma$ and hence[4]:

$$\sigma = r/2(P_{max})_{h=0} \quad \text{(I.47)}$$

The density of the fluid can be derived from the slope (=ρg) of the line.

I.4.4. Capillary rise Technique

This technique has frequently been used to determine surface tension of organic liquids, but due to inherent practical limitations, it has rarely been used for molten metal systems. The free surface of a liquid confined between the walls of a container will, in general, be curved and it follows from the Laplace equation that across the liquid/gas interface there exists a pressure differential whose magnitude will be related to the principal radii of curvature. If a capillary tube (radius r) is immersed in a liquid pool (density ρ_L) then within the tube, a liquid meniscus will be produced which depending on the prevailing wetting conditions, can "lie above or below the surface level of the liquid in the pool. Figure (I.11) illustrates the situation for a system in which the liquid wets ($\theta < 90°$) the material of the tube. At the equilibrium height h_0, the hydrostatic pressure of the liquid column equals the pressure difference across the meniscus, i.e. for a meniscus with spherical profile (r small)[4].

$$2\sigma/R = h_0 g\Delta\rho \approx h_0 g\rho_L \qquad \text{(I.48)}$$

Where R is the radius of curvature and $\Delta\rho$ the difference in density between liquid and gas. In the general case, the radius of curvature of the spherical meniscus is related to the radius of the capillary tube by[4]:

$$R = r/\cos\theta \qquad \text{(I.49)}$$

and thus :

$$\sigma = \left(\frac{h_0 g\rho_L r}{2\cos\theta}\right) \qquad \text{(I.50)}$$

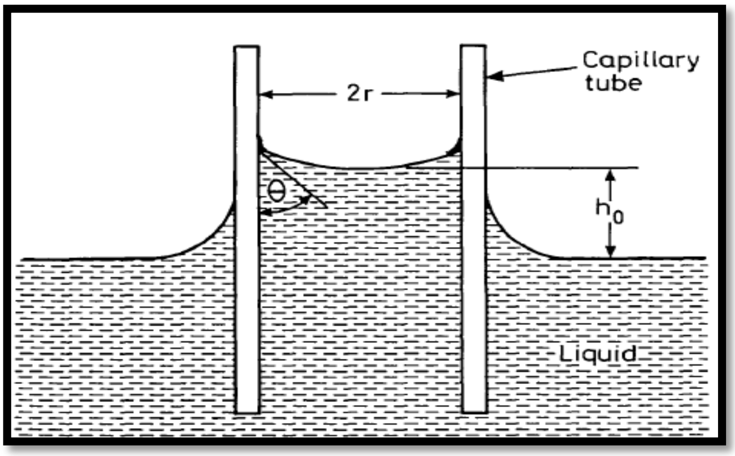

Fig.I.11: Capillary rise method for determining surface tension[4]

With non-wetting systems, e.g. Hg/glass, the liquid meniscus is convex and the equilibrium position in the capillary tube will be below the surface level of the liquid pool (capillary depression); Obviously , in this case, measurement of h_0 is considerably more difficult than with a wetting system, because of the opacity of the metal. The most accurate values for σ are obtained by this technique when $\theta = 0$ [4] .

I.4.5. Drop **Volume (Drop Weight) Technique**

The drop-volume method is used to measure surface and interfacial tensions of liquids by a detachment method[11]. The experimental basis of this technique, is to produce slowly at the end of a capillary tube, a liquid drop which increases in size until it ultimately detaches and is collected in a container. This procedure is repeated a number of times until sufficient material has accumulated to establish an accurate value for the mean weight ω per drop (figure (I.12)). Under ideal circumstances, the gravitational force acting on the drop at the point of detachment would be equal to the opposing surface tension force, in accord with Tate's law, i.e[4].;

$$\omega_{ideal} = 2\pi r\sigma \qquad \text{(I.51)}$$

where *r* is the radius of the tube.

The detached drop always leaves behind a considerable residue of liquid, the actual weight of a drop that is measured will need to be corrected by a factor *f* in that[11]:

$$\omega_{actu} = f\ \omega_{ideal} \qquad \text{(I.52)}$$

The factor *f* is a function of the ratio $r/V^{1/3}$ (where V is the volume of the drop), and the usual procedure is to determine *V* from the drop weight (provided the density is known with sufficient accuracy).

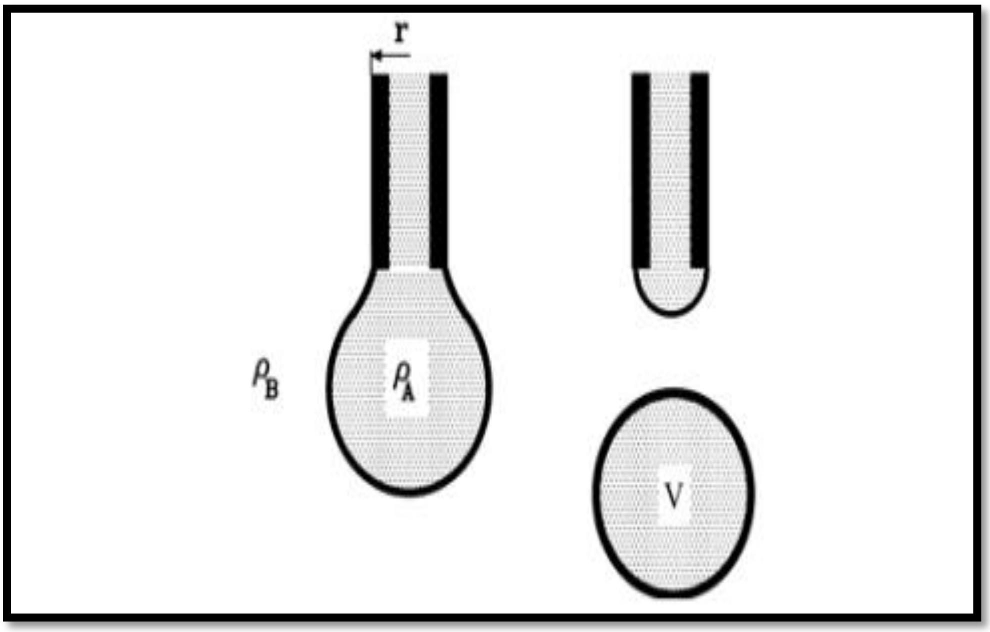

Fig.I.12: Schematic illustration of drop volume or weight method[6]

I.4.6. The Du Nouy ring Technique

The Du Noüy ring method is used to measure static surface and interfacial tensions of liquids . The apparatus required to carry out this type of measurement consists of a vessel containing the liquid(s) to be analyzed and a ring, which is attached to a sensitive force-measuring device (figure I.13). The vessel is capable of being moved upward and downward in a controlled manner while the position of the ring is kept constant[20].

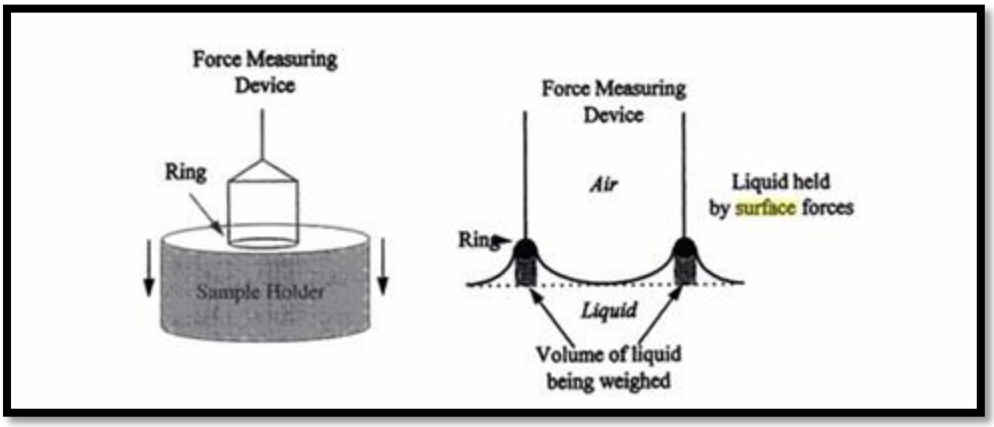

Fig.I.13: Du Noüy ring method of determining the interfacial and surface tension of liquids[20]

Initially, the vessel is positioned so that the ring is submerged just below the surface of the liquid being analyzed. It is then slowly lowered and the force exerted on the ring is recorded.

As the surface of the liquid moves downward, some of the liquid "clings" to the ring because of its surface tension (figure I.13). The weight of the liquid that clings to the ring is recorded by the force-measuring device and is related to the force that results from surface tension. The Du Noüy ring method is usually used in a "detachment" mode. The vessel is lowered until the liquid clinging to the ring ruptures and the ring becomes detached from the liquid[20].

The force exerted on the ring at detachment is approximately equal to the surface tension multiplied by the length of the ring perimeter:

$$F = 4\pi\, r\, \sigma \qquad \text{(I.53)}$$

Hence ,

$$\sigma = \frac{F}{4\pi r} \qquad \text{(I.54)}$$

where *r* is the radius of the ring.

For accurate measurements, it is important that the bottom edge of the ring be kept parallel to the surface of the fluid and that the contact angle between the liquid and the ring is close to zero. Rings are usually manufactured from platinum or platinum-iridium because these give contact angles that are approximately equal to zero. The Du Noüy ring method can be used to determine surface tensions to an accuracy of about 0,1 $\mathrm{mN.m^{-1}}$[20].

I.4.7. Wilhelmy Plate Technique

The Wilhelmy plate method presents analogies with the Du Noüy ring method. The main principle is the same. The plate, which plays the role of the ring, is just in contact with the liquid to be analyzed (Fig. I.14)[21] .

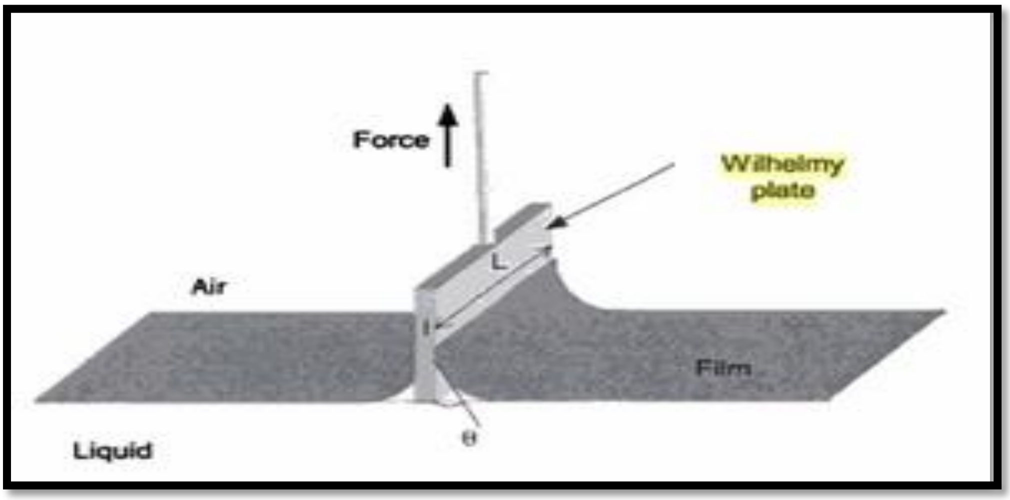

Fig.I.14: Schematic representation of Wilhelmy plate device. L: length of the plate, *l*: thickness of the plate, θ: angle between the plate and the interface [21].

A certain amount of liquid moves up the plate in relation to its surface tension and its density. The weight of the liquid moving up is balanced by the surface tension and can be measured. Relationships between the force and the surface tension take into account the dimensions (length and thickness) of the plate and the contact angle, as shown in the following equation[21]:

$$\sigma = \frac{F}{(2L+2l)cos\theta} \qquad (I.55)$$

here L and l are the length and thickness of the plate and θ is the contact angle.

The plate mass is tarred before the measurement. Materials are chosen in order to give a contact angle close to zero. Hence, the analysis is simpler if platinum, whose surface is fine roughened to support better moistening, is used, for example. The Wilhelmy plate method presents an important advantage. The detachment of the plate from the liquid is not necessary. For this reason, the adsorption kinetics of surfactants is not an important cause of errors. The Wilhelmy-plate method is simple and no correction factors are required. Care has to be taken to keep the plates clean and prevent contamination in air[21].

I.4.8. The spinning dropTechnique

Bernard Vonnegut in 1942 proposed the rotating bubble (spinning drop) method for surface and interfacial tension determinations. In this method a small bubble of an immiscible liquid “A” suspended in a more dense liquid “B” and all the system is put under rotation about a horizontal axis (Fig. I.15), because of the centrifugal forces “A” to find an equilibrium position will migrate to the center forming a drop astride the spinning axis. As the centrifugal force increases to a sufficiently high value, the drop changes to a cylindrical shape. The surface or interfacial tensions are calculated using equation (I.56) suggested by Vonnegut under the following considerations. The elongation of the bubble stops when the centrifugal forces are balanced by the surface tension forces, assuming that the length L of the bubble is large compared with the radius ($L>R$) so it can be treated like a circular cylinder with hemispherical ends and a negligible effect of gravity at increased speeds of rotation, then it is possible to write an expression for the total energy of the bubble and solve it for the equilibrium shape with the minimum energy[6] :

$$\sigma = \frac{\Delta\rho\omega^2}{4}R^3 \qquad (I.56)$$

where σ is the interfacial tension, $\Delta\rho$ is the difference between the densities of the droplet and of the surrounding fluid, ω is the angular velocity and R is the cylinder radius.

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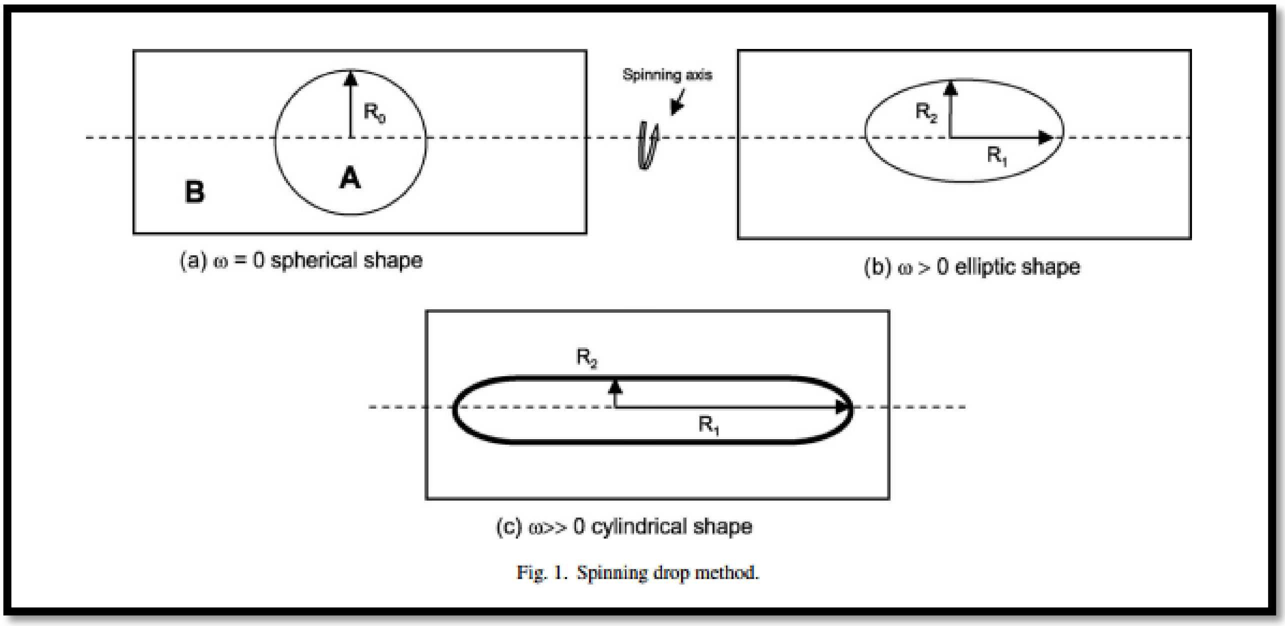

Fig.I.15: Spinning drop method [6].

The spinning drop method is usually preferred for the accurate measurements of surface tensions below 10^{-2} mN/m. It refers to either using the fluids with low interfacial tension or working at very high angular velocities. This method is widely used in many different applications such as measuring the interfacial tension of polymer blends and copolymers[6]. A device used for such measurements is called a "*spinning drop tensiometer*".

I.5. Angle of contact

The contact angle is defined as the angle at which a liquid/vapor interface meets the solid surface. The advantage of exploiting the contact angle to describe the wetting property of a liquid on a solid is intuitive. The disadvantage is the lack of representation on the energy variation during the wetting process. The contact angle of a drop on a solid surface is a result of the equilibrium among the surface tensions of the solid/gas/liquid interfaces[22].

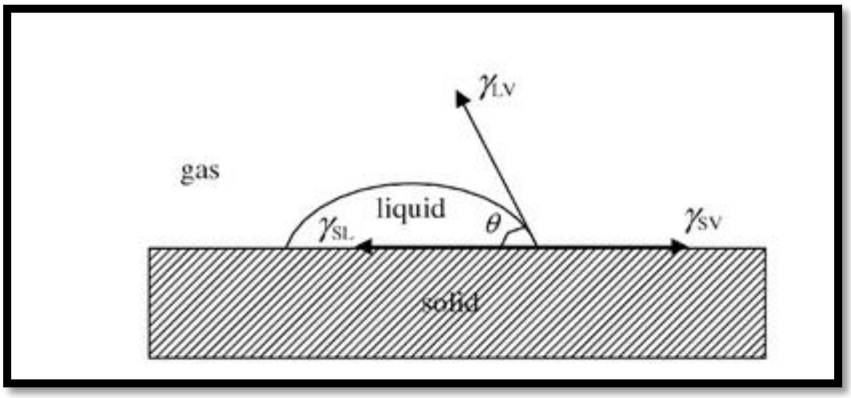

Fig.I.16: definition of the contact angle[22] .

The equilibrium makes the whole energy of lowest and thus leads the droplet to be in the stable or metastable surface can be characterized by the Young's equation [22]:

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos\theta \qquad \text{(I.57)}$$

$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}} \qquad \text{(I.58)}$$

in which σ_{SV} , σ_{SL} and σ_{LV} represent solid/gas, solid/liquid and liquid/gas interface tensions, respectively. The angle θ is called the balance contact angle or the intrinsic contact angle of the material.

Young's equation is the foundation of research on the solid/liquid wetting interaction. The value of the contact angle θ is the criterion of the wetting property[22]:

- $\theta = 0$ entirely wetting; liquid spreads on the solid surface .
- $0 < \theta < 90^\circ$ liquid wets the solid; the wetting property is better for smaller θ.
- $90^\circ < \theta < 180^\circ$ liquid does not wet the solid
- $\theta = 180^\circ$ completely unwetting ; liquid turns to be a ball on the solid.

It should be pointed out that the application condition of the Young's equation is the ideal surface. In other words, the solid surface is smooth, isotropic, deformed (under the impact of the vertical component of the liquid surface tension) and has a homogeneous component; only on surfaces like this the liquid has a settled stable contact angle.

If there is no interaction between the solid and liquid, then[23]

$$\sigma_{SL} = \sigma_{SV} + \sigma_{LV} \quad \text{(I.59)}$$

that is, $\theta = 180°$ ($\cos\theta = -1$).

If there is strong interaction between solid and liquid (maximum wetting), the latter spreads until Young’s equation is satisfied (θ = 0) and

$$\sigma_{LV} = \sigma_{SV} - \sigma_{SL} \qquad \text{(I.60)}$$

The liquid spreads spontaneously on the solid surface (entirely wetting). When the surface of the solid is in equilibrium with the liquid vapor, then one must consider the spreading pressure π_e. As a result of the adsorption of the vapor on the solid surface, its surface tension σ_s is reduced by π_e, that is [23]:

$$\sigma_{SV} = \sigma_s - \pi_e \qquad \text{(I.61)}$$

and Young’s equation can be written than as:

$$\sigma_{LV} \cos\theta = \sigma_s - \sigma_{SL} - \pi_e \qquad \text{(I.62)}$$

But In a real system, however,- a range of contact angles is usually obtained instead (figure I.17). The upper limit of the range is the advancing contact angle θ_a , which is the contact angle found at the advancing edge of a liquid drop. The lower limit is the receding contact angle θ_r , which is the contact angle found at the receding edge. The difference between the advancing and receding contact angles is known as the contact angle hysteresis θ_{hyst} [23]:

$$\theta_{hyst} = \theta_a - \theta_r \qquad \text{(I.63)}$$

Contact angle hysteresis can be due to roughness and heterogeneity of a solid surface. If roughness is the primary cause, then the measured contact angles are meaningless in terms of Young’s equation. On very rough surfaces, contact angles are larger than on chemically identical, smooth surfaces.[22]

I.5.1.Contact Angles and Work of Adhesion

When liquid comes in contact with a solid, the solid–liquid interface is created while solid–vapor and liquid–vapor interfaces are destroyed. The work of adhesion between the liquid and the solid per unit area is given by the Dupré equation[24]:

$$W= \sigma_{SV} + \sigma_{LV} - \sigma_{SL} = \sigma_{LV}(1 + \cos\theta) \qquad \text{(I.64)}$$

Chapter II

Calculation of the surface tensions of the system

II.1. Introduction

The chemical composition of the surface is one of the most important properties that must be known in order to determine other surface phenomena. Based on thermodynamics, it can be convincingly demonstrated that the surface composition can be very different from that of volume for most multi-component systems. In many important surface phenomena, the chemical composition of the uppermost layer controls the surface properties and not the composition of the volume. It is therefore necessary to develop thermodynamic models that predict the surface composition of multi-component systems based on volume composition and temperature [10]. Among the surface properties, the surface tension of metal alloys is very important in witting interfacial phenomena including many processes in metallurgy especially in welding [9].

In this chapter we propose a thermodynamic approach to calculate the surface tension and the surface segregation in liquid binary systems. For 4 types of liquid binary system that are Cu-Ni and Fe-Ni and Fe-Cu and also Al-Ni are investigated. These are the widely encountered systems and available in the literature that deals with the phenomenon of surface tension in binary metal alloys [2].

II.2. Definitions

II.2.1. Molar area

Because of differences in the densities of various materials, they will have differing numbers of atoms occupying a unit area. Let us define an area, A, as the area occupied by Avogadro's number of atoms, N. The atomic volume V is given by:

$$V_a = \frac{V_i^{(l)}}{N_i} \qquad \text{(II.1)}$$

where $V_i^{(l)}$ is the molar volume of the element i in the liquid phase, given by:

$$V_i^{(l)} = \frac{M_i}{P_i^{(l)}} \qquad \text{(II.2)}$$

where M_i is the molar mass of the element i and $P_i^{(l)}$ is its density for the liquid phase.

Thus, the surface per atom will be written of such:

$$\omega = f\,V_a \qquad \text{(II.3)}$$

Where f is a structure factor that depends on the compactness of the interface of the mono system component [25]

The molar area of an element *i* in a liquid phase is therefore given by

$$\omega_{0i}^{l} = f N_A^{1/3} V_{(l)}^{2/3} \qquad \text{(II.4)}$$

where f = 1,09 [26]

II.2.2.Interaction parameter of the liquid solution (the miscibility energy)

Kaufman and Bernstein [25] calculate the interaction parameter of the liquid phase (the miscibility energy) is being the sum of two terms:

$$L = e_0 + e_p \qquad \text{(II.5)}$$

where e_p is the contribution of the internal pressure translated by solubility parameters of the two constituents of the binary system and e_0 is a term related to the electronic interactions between the components of the binary system

Kauffmann and Bernstein give the term e_p by:

$$e_p = 0.3(V_1 + V_2)\left[\sqrt{-\frac{H_1}{V_1}} - \sqrt{-\frac{H_2}{V_2}}\right]^2 \qquad \text{(II.6)}$$

where 0.3 is a correction factor, H is the sublimation enthalpy, V is the molar volume of the solid.

For transition metals the expression (II.6) gives unsatisfactory results. So Kauffman adopt another approach based on sublimation enthalpies.

$$e_0 = -23060\bar{n}\left(X_i - X_j\right)^2 \qquad \text{(II.7)}$$

Where $\bar{n} = 5$ and X_i and X_j are the electronegativities of the two constituents.

Kauffmann has determined the expression of e_0 which is based on the concept of heats of sublimation [25]:

$$e_0 = 2\left\{\phi_1\left(\frac{i+j}{2}\right) - \frac{1}{2}\left[\phi_1(i) + \phi_1(j)\right]\right\} \text{(II.8)}$$

Where ϕ_1 is the enthalpy of sublimation.

in the following figure the result obtained per Boutassouna which represents the extrapolation of Kaufman method

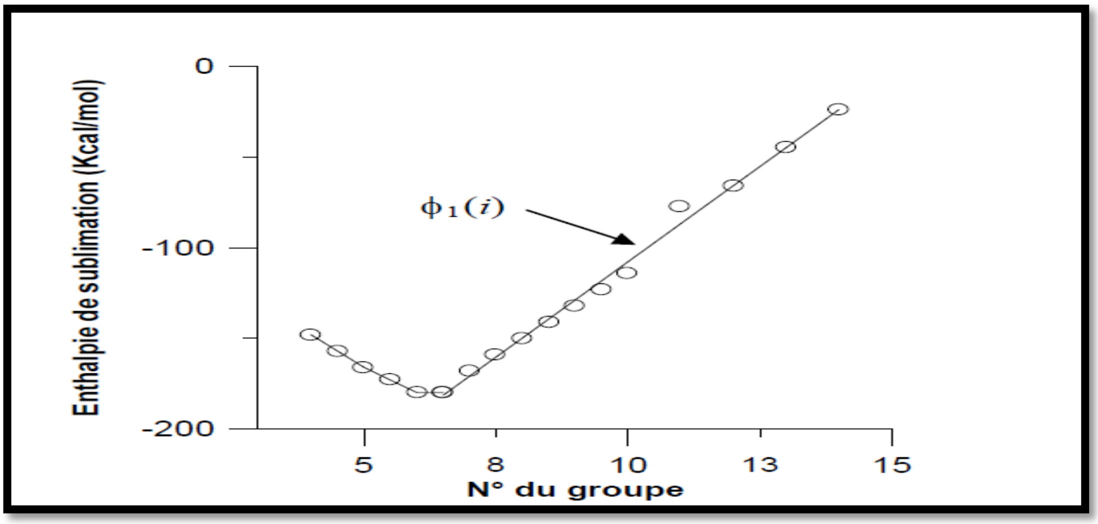

Fig.II.1: Variation of the sublimation enthalpy H as a function of the group number (from the group of Ti (No. 4) to the group of Ge (No. 14).[25]

II.3. Physical properties of the studied systems and their components

Table (II.1) presents the different properties and magnitudes of the components of these alloys.

Table II.1: Physical properties of pure metals used in the systems studied

Element / Magnitudes	Cu	Fe	Ni	Al
ρ (g/cm^3)	8.02	6.98	7.51	2.37
$\omega_{0i}^{(l)}(m^2$/mol)	36583	37831	36233	46514
$\sigma_{0i}^{(l)}$(J/m^2)[26]	1.36	1.872	1.778	0.914
M (g/mol)	63.55	55.84	58.69	26.98
$V^{(l)}(cm^3$/mol)	7.92	8	7.81	11.38

And table (II.2) presents the miscibility energies of the volumes. Miscibility energies of the surface.

Table II.2: Volume and surface miscibility energies for both systems.

Systems / Magnitudes	Cu-Fe	Cu-Ni	Fe-Ni	Ni-Al
$\Omega^{(l)}$ (J/mol)	-93498.24	3799	2360	-10454
$\Omega^{(ls)}$(J/mol)	- 62332.16	2532.66	1573.33	-6969.33

II.4. Thermodynamic model

Thermodynamic relations for the surface tension can be obtained based on the assumption that the surface can be treated thermodynamically as a phase separate from the bulk liquid phase.

The chemical potential of each component ν=i, j is:

$$\mu_\nu^l = \mu_{0\nu}^l + RTlna_\nu^l \quad \text{(II.8)}$$

where a_ν^l is the thermodynamic activity of the component νat the bluk of the phase i and which is defined by $a_\nu^l = x_\nu^l \gamma_\nu^l$, where γ_ν^l , is the thermodynamic activity of the component And Where the index '0' indicates that the physical quantity considered is relative to the pure state of the component in question.

At the surface region, noted s, the chemical potential will have a similar expression to (II.8) with an additional term that of mechanical surface work, namely:

$$\mu_\nu^{sl} = \mu_{0\nu}^{sl} + RTlna_\nu^{sl} - \omega_{0\nu}\,\sigma \quad \text{(II.9)}$$

Where a_ν^{sl} is the thermodynamic activity of the component θ at the surface of the phase l and which is defined by $a_\nu^{sl} = x_\nu^{sl}\ \gamma_\nu^{sl}$, where γ_ν^{sl} is the surface thermodynamic activity coefficient; σ is the surface is tension and $\omega_{0\nu}$ is the molar area of the component.

At a fixed temperature T and constant pression, the equilibrium condition between surface and volume for a constituent ν = i, j is expressed by the equality of chemical potential of a component in both sides bulk and surface, so:

$$\mu_v^l = \mu_v^{sl} \qquad \text{(II.10)}$$

Using the relation (II.3), the equilibrium condition can be expressed by:

$$\mu_{0v}^l + RTlna_v^l = \mu_{0v}^{sl} + RTlna_v^{sl} - \omega_{0v}\,\sigma \qquad \text{(II.11)}$$

This leads to:

$$\omega_{0v}\,\sigma = \left(\mu_{0v}^{sl} - \mu_{0v}^l\right) + RTln\,\frac{a_v^{sl}}{a_v^l} \qquad \text{(II.12)}$$

For a pure component, Chemical potentials at surface can be expressed like in the bulk plus a surface term:

$$\mu_{0v}^{sl} = \mu_{0v}^l + \omega_{0v}\,\sigma_{0v} \qquad \text{(II.13)}$$

Then expression (II.13) can be written as :

$$\omega_v\,\sigma = \omega_{0v}\,\sigma_{0v} + RTln\,\frac{a_v^{s\varphi}}{a_v^{\varphi}} \quad \text{(II.14)}$$

We suppose that: $\omega_v = \omega_{0v}$, the surface tension of the liquid binary system is:

$$\sigma = \sigma_{0v} + \frac{RT}{\omega_{0v}} ln\,\frac{a_v^{sl}}{a_v^l} \qquad \text{(II.15)}$$

From the expression (II.8), the following relation can be drawn from the surface tension:

$$\begin{cases} \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}} ln\,\frac{a_i^{sl}}{a_i^l} \\ \sigma = \sigma_{0j} + \frac{RT}{\omega_{0j}} ln\,\frac{a_j^{sl}}{a_j^l} \end{cases} \qquad \text{(II.16)}$$

By eliminating σ from the system of equation (II.16), we obtain the relation which links surface and volume molar fractions via thermodynamic activities:

$$\frac{a_i^{sl}}{(a_j^{sl})^{\lambda}} = K\,\frac{a_i^l}{(a_j^l)^{\lambda}} \qquad \text{(II.17)}$$

Where $K = \exp\left[\frac{(\sigma_{0j}-\sigma_{0i})\omega_{0i}}{RT}\right]$ and $\lambda = \omega_{0i}\,/\omega_{0j}$ (II.18)

When the mole fractions of surfaces are determined from the equation (II.17), we can then calculate the tensions surfaces in (II.18). The main problem of this procedure of calculations is how to express the thermodynamic activities via the surface molar fraction?

Such a problem is very difficult to solve since the real solutions are very difficult to describe by thermodynamics. In literature some models are adopted [1-9]. We chose two of the simpler of them:

- The ideal solution
- The regular solution

II.4.1. Case of the Ideal Solution:

In the case of the ideal solution, the activity at the volume and the surface of the phase l are equal to their molar fractions: $a_v^{sl} = x_v^{sl}$ and $a_v^{l} = x_v^{l}$. Equations (II.16) will be written as follows:

$$\begin{cases} \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}} ln \ \frac{x_i^{sl}}{x_i^{l}} \\ \sigma = \sigma_{0j} + \frac{RT}{\omega_{0j}} ln \ \frac{x_j^{sl}}{x_j^{l}} \end{cases} \qquad \text{(II.19)}$$

We know that in binary system: $x_j^l = 1 - x_i^l$ and, $x_j^{sl} = 1 - x_j^{sl}$.

So, equations (II.19) will be expressed by:

$$\begin{cases} \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}} ln \ \frac{x_i^{sl}}{x_i^{l}} \\ \sigma = \sigma_{0j} + \frac{RT}{\omega_{0j}} \ ln \ \frac{1-x_i^{sl}}{1-x_i^{l}} \end{cases} \qquad \text{(II.20)}$$

By elimination of the surface tension in the system equations (II.20), we obtain the expressions of the surface molar fractions as a function of its bulk :

$$\frac{x_i^l}{x_i^{sl}} \frac{(1-x_i^{sl})^{\lambda}}{(1-x_i^{l})^{\lambda}} - K = 0 \qquad \text{(II.21)}$$

Knowing the value of the surface molar fraction, we can use one of the tow equations in (II.22) we can calculate the surface tension of liquid system.

II.4.2. Case of the regular solution

In the case of the regular solution the activity is written as follows:

- For volume $a_v^l = x_v^l \, exp\left(\frac{\Omega(1-x_v^l)^2}{RT}\right)$
- For surface $a_v^{sl} = x_v^{sl} \, exp\left(\frac{\Omega(1-x_v^{sl})^2}{RT}\right)$

The relation of the surface tensions of the liquid phase will have for expressions:

$$\begin{cases} \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}} \, ln \, \frac{x_i^{sl}}{x_i^l} + \frac{\Omega^s(1-x_i^{sl})^2}{\omega_{0i}} - \frac{\Omega(1-x_i^l)^2}{\omega_{0i}} \\ \sigma = \sigma_{0j} + \frac{RT}{\omega_{0j}} ln \, \frac{x_j^{sl}}{x_j^l} + \frac{\Omega^s(1-x_j^{sl})^2}{\omega_{0j}} - \frac{\Omega(1-x_j^l)^2}{\omega_{0j}} \end{cases} \tag{II.23}$$

in binary systems: $x_j^l = 1 - x_i^l$ and $x_j^{sl} = 1 - x_j^{sl}$, so equation (II.23) will be written as:

$$\begin{cases} \sigma = \sigma_{0i} + \frac{RT}{\omega_{0i}} \, ln \, \frac{x_i^{sl}}{x_i^l} + \frac{\Omega^s(1-x_i^{sl})^2}{\omega_{0i}} - \frac{\Omega(1-x_i^l)^2}{\omega_{0i}} \\ \quad \sigma = \sigma_{0j} + \frac{RT}{\omega_{0j}} ln \, \frac{1-x_i^{sl}}{1-x_i^l} + \frac{\Omega^s {x_i^{sl}}^2}{\omega_{0j}} - \frac{\Omega {x_i^l}^2}{\omega_{0j}} \end{cases} \tag{II.24}$$

By elimination of the surface tensions of the liquid solutions, we obtain an expression which allows us to determine the surface molar fractions as a function of that of the volume one in liquid binary system:

$$\omega_{0i}\,(\sigma_{0j} - \sigma_{0i}) + RT\left[-\frac{1}{\omega_{0i}} \ln \frac{x_i^{sl}}{x_i^l} + \frac{1}{\omega_{0j}} \ln\left(\frac{1-x_i^{sl}}{1-x_i^l}\right)\right] - \Omega^s\left(1 - x_v^{sl}\right)^2 + \Omega\left(1 - x_i^l\right)^2 + \gamma\Omega^s {x_v^{sl}}^2 - \gamma\Omega {x_i^l}^2 = 0 \tag{II.25}$$

This equation can be written for the two liquid phase , such that:

$$\frac{x_i^l}{x_i^{sl}}\left(\frac{1-x_i^{sl}}{1-x_i^l}\right)^{\gamma} - \exp\left[-\frac{1}{RT}\left(-\Omega^s\left(1 - x_i^{sl}\right)^2 + \Omega\left(1 - x_i^l\right)^2 + \gamma\Omega^s {x_i^{sl}}^2 - \gamma\Omega {x_i^l}^2 + \omega_{0i}\,(\sigma_{0j} - \sigma_{0i})\right)\right] = 0 \tag{II.26}$$

The resolution of equation (II.26) makes it possible to determine the fractions for the four systems the case of the regular solution model which will be used for calculating the surface tensions of liquid solutions from the system of equations (II.24).

To calculate the surface tension of liquid binary alloys and the surface fraction molar in both considered solution models, we first need to know some physical properties of pure components and the value of the miscibility energy.

II.5. Calculation of the surface tensions of the studied systems

In the next section, we will calculate the surface tension of liquid solutions, each one separately of the four binary systems (Cu-Ni and Fe-Cu, Fe-Ni and Al-Ni) according to the two models (ideal and regular). The surface molar fraction is first calculated than the surface tension. After this, we compare our results with the experimental ones reported in literature [2, 9].

In the work [2] the surface tension was calculated for a binary AB liquid metallic solution using Butler equation:

$$\sigma_{AB}(T) = \sigma_A + \frac{RT}{S_A} ln\left(\frac{1-c_B^S}{1-c_B^B}\right) + \frac{1}{S_A} \times \{\Delta G_A^S(T, c_A^S) - \Delta G_A^B(T, c_A^B)\}$$

$$= \sigma_B + \frac{RT}{S_B} ln\left(\frac{c_B^S}{c_B^B}\right) + \frac{1}{S_B} \times \{\Delta G_B^S(T, c_B^S) - \Delta G_B^B(T, c_B^B)\} \qquad \text{(II.27)}$$

where S_A,S_B: surface areas in a monolayer of pure liquid and B. c_A^B, c_B^B : mole fractions of A and B respectively in the bulk phase, and c_A^S,c_B^S: mole fractions of A, B in the surface phase. ΔG_A^B,ΔG_B^B denote the partial excess Gibbs energy of A, B, in the bulk and. ΔG_A^S,ΔG_B^S are the partial excess Gibbs energy of A, B, in the surface layer and $\Delta G_X^S \approx \frac{3}{4}\Delta G_X^B$. The expressions of partial excess Gibbs energies are written according a sub-regular model. These excess quantities can be found from the excess molar Gibbs energy for the liquid binary solution according using the formula: X= A or B.

$$\Delta G_X = \Delta G + (1 - c_X)(\frac{\partial \Delta G}{\partial c_X}) \qquad \text{(II.28)}$$

The following tables show how to calculate thermodynamic excess potentials for the three binary liquid systems.

TABLE.II.3: Thermodynamic potentials ΔG, used in Equation(II.28). For element X, the partial free enthalpy of mixing $\Delta G_X$is related to the free enthalpy of mixing ΔG , according to [2]:

System	Excess Gibbs energy ΔG, J/mole
Ni-Cu	$\Delta G = c_{Ni}.c_{Cu}[(12048 + 1{,}29T) + (-1861{,}6 + 0{,}942T)(2c_{Ni} - 1)]$
Ni-Fe	$\Delta G = c_{Ni}.c_{Fe}[(-8368 + 2{,}72T)c_{Fe} + (-32217 + 9{,}205T)c_{Ni}]$
Fe-Cu	$\Delta G = c_{Cu}.c_{Fe}[(-36087{,}98 - 2{,}33T) + (324{,}53 - 0.033T)(2c_{Cu} - 1) + (10355{,}39 - 3{,}603T)(2c_{Cu} - 1)^2]$

Calculated surface tensions via expression for the three considered liquid systems are resumed in the table II.4.

Table II.4: surface tension of elements [2]

element	Surface tension σ
Cu	1,29
Fe	1,92
Ni	1,77

For the system Al-Ni, we compare it to the results of another article[9] .

II.5.1.Calculation of surface tensions for system Cu-Ni

We calculate the molar fraction of surface of as a function of the molar fraction of volume (from 0 to 100%) at T=1546.15 K. This temperature was chosen the same as in the experimental work [§§] in order to compare our calculation results with the experimental ones.

We put i = Ni, j = Cu. So for ideal solution model, equation (II.21) becomes:

$$\frac{x_{Ni}^{l}}{x_{Ni}^{sl}}\frac{(1-x_{Ni}^{sl})^{\lambda}}{(1-x_{Ni}^{l})^{\lambda}} - K = 0 \qquad \text{(II.29)}$$

The resolution of equations (II.29) makes it possible to determine the molar fractions of the liquid surface phase of Ni in the ideal solution case. For the regular solution model, we use the (II.26) which becomes:

$$\frac{x_{Ni}^{l}}{x_{Ni}^{sl}}\left(\frac{1-x_{Ni}^{sl}}{1-x_{Ni}^{l}}\right)^{\gamma} = exp(-\frac{1}{RT}[-\Omega^{s}\left(1 - x_{Ni}^{sl}\right)^{2} + \Omega\left(1 - x_{Ni}^{l}\right)^{2} - \gamma\Omega^{s}{x_{Ni}^{sl}}^{2} + \gamma\Omega{x_{Ni}^{l}}^{2} + \omega_{0Ni}\,(\sigma_{0Cu} - \sigma_{0Ni}\,)]) \qquad \mathit{(II.30)}$$

The resolution of equation (II.30) makes it possible to determine the molar fractions of the liquid surface phases of Ni in the regular solution.

Figure (II.2) shows the variation of the molar surface fractions of the liquid phase as a function of the molar fractions of the volume of the liquid for the ideal solution (the dashed line) and regular solution (the solid line).

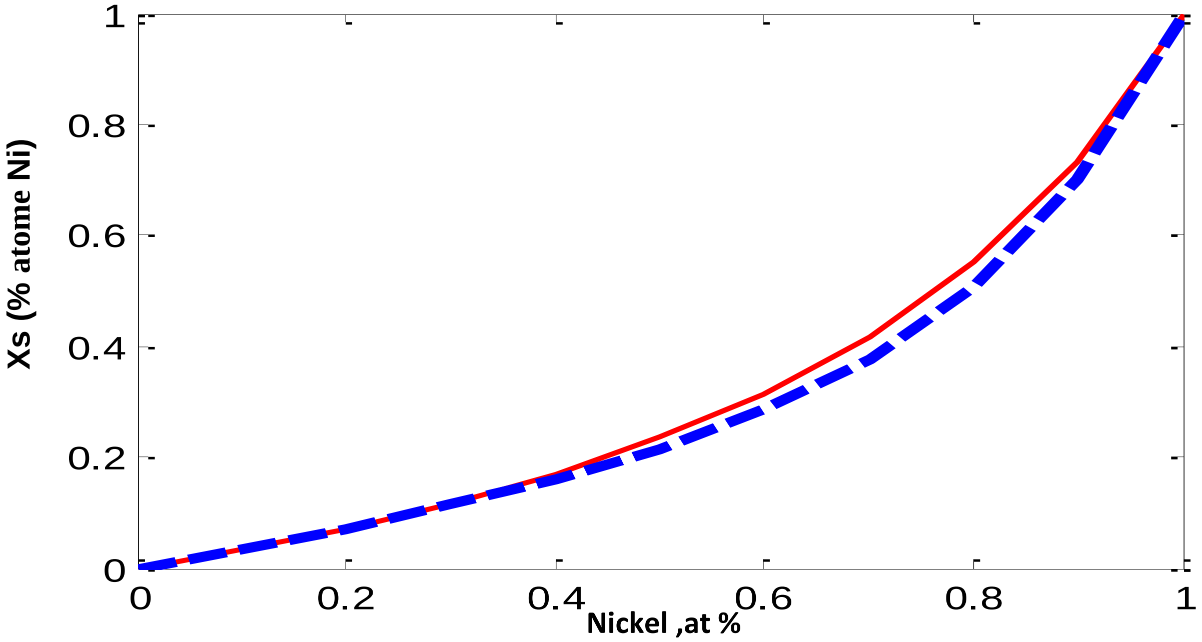

Fig.II.2: Variation of the molar fractions of surface of Ni as a function of its bulk molar fraction for Cu-Ni system at T= 1546.15 K.

Figure II.2 shows that Cu will segregate at the surface of Cu-Ni. Indeed, it's known that in liquid phases, the surfactant element has a tendency to segregate at the surface ($\sigma_{Cu}^{l} < \sigma_{Ni}^{l}$, table II.1). This segregation increased from X_{Cu}=100% to X_{Cu}=40% and decreased from X_{Cu}=40% to X_{Cu}=0% (pure Ni).

Comparing the results gives by the two considered models, we remark that the miscibility energy gives a weak contribution compared to the ideal case, which implies that the effect of the surface tensions is predominant.

For calculation the surface tension of liquid binary alloy Cu-Ni in ideal solution we use the equations systems (II.20) which becomes:

$$\begin{cases} \sigma = \sigma_{0Ni} + \frac{RT}{\omega_{0Ni}} ln \frac{x_{Ni}^{sl}}{x_{Fe}^{l}} \\ \sigma = \sigma_{0Cu} + \frac{RT}{\omega_{0Cu}} ln \frac{1-x_{Cu}^{sl}}{1-x_{Cu}^{l}} \end{cases} \qquad \text{(II.29)}$$

For calculation the surface tension of alloy Cu-Ni in the regular solution, equation (II.21) becomes:

$$\begin{cases} \sigma = \sigma_{0\mathrm{Ni}} + \frac{RT}{\omega_{0\mathrm{Ni}}} \ln \frac{x_{\mathrm{Ni}}^{sl}}{x_{\mathrm{Ni}}^{l}} + \frac{\Omega^{s}(1-x_{\mathrm{Ni}}^{sl})^{2}}{\omega_{0\mathrm{Ni}}} - \frac{\Omega(1-x_{\mathrm{Ni}}^{l})^{2}}{\omega_{0\mathrm{Ni}}} \\ \sigma = \sigma_{0\mathrm{Cu}} + \frac{RT}{\omega_{0\mathrm{Cu}}} \ln \frac{1-x_{\mathrm{Cu}}^{sl}}{1-x_{\mathrm{Cu}}^{\varphi}} + \frac{\Omega^{s}{x_{\mathrm{Cu}}^{sl}}^{2}}{\omega_{0\mathrm{Cu}}} - \frac{\Omega {x_{\mathrm{Cu}}^{l}}^{2}}{\omega_{0\mathrm{Cu}}} \end{cases} \qquad \text{(II.30)}$$

Figure (II.3) shows the variation of the surface tensions of the Cu-Ni liquid alloys at 1546.15 K is plotted as a function of the Ni content for the ideal solution (solid line) and regular solution (the dashed line).

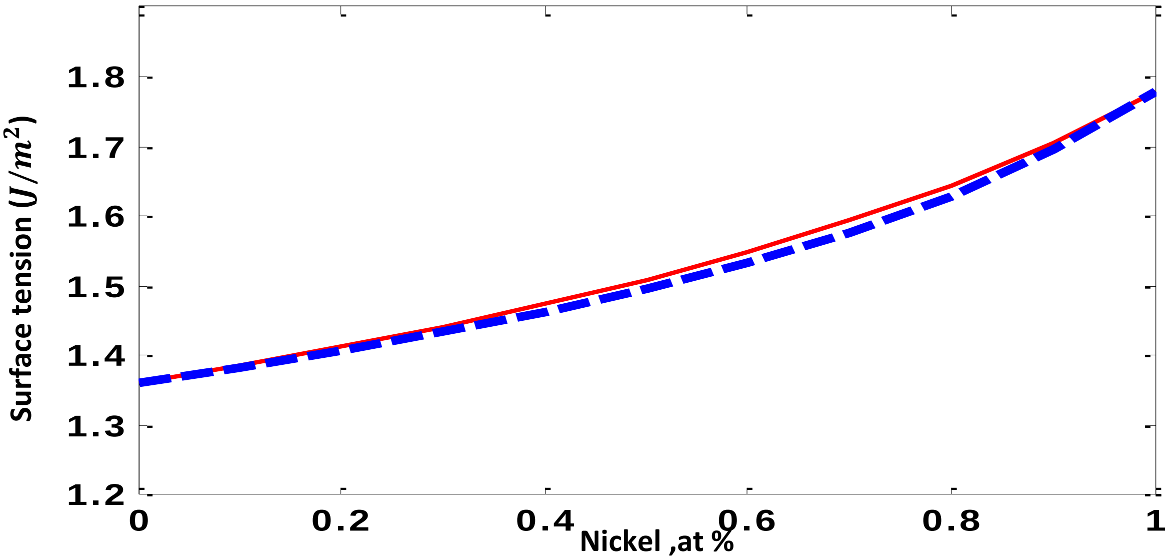

Fig .II3: Variation of surface tension of liquid system Cu-Ni as a function

of the molar fractions of bulk at T=1546.15K.

In Figure (II.3)) we observe in both of model approximately linear variation of surface tension with a composition between the surface tension limits for each component of pure metal in binary alloys where surface tension of copper increases sharply with increasing Ni content, and the small difference between the surfaces tensions of two models is due to the weak effect of the miscibility energy.

The comparison of surface tension the calculated and experimental of the Cu-Ni system is shown in Figure II. 4.

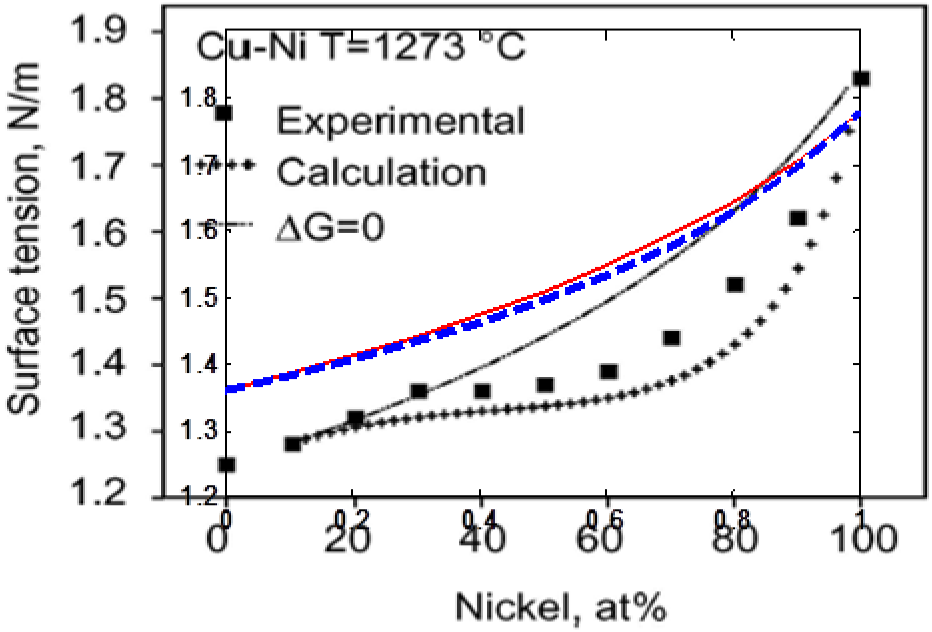

Fig.II4: Comparison between surface tension of the calculated

and experimental[2] of the Cu-Ni system.

We remark that our calculated curves has the same behaviour with the calculated ones by [2] and approximately with the experimental results. The difference between values is due to the fact that in our model we didn’t take in account the variation of the liquid surface tension with temperature. At the other hand, our model of solution is simple comparing with the sub-regular model using in [2] (Table II.3).

II.5.2.Calculation of surface tensions for system Fe-Ni

We calculate the surface molar fraction of liquid Fe as a function of the molar fraction of volume (from 0 to 100%) at T=1546.15 K. This temperature is used in experimental work [2].

Equations using in calculations of the surface segregation and the surface tension in Fe-Ni are the same for the Cu-Ni system (equations II.29 and II.30).

Figure (II.5) shows the variation of the surface molar fractions of the liquid binary phase as a function of the molar fractions of the volume of the liquid according to the ideal solution model (marked by solid line)   and regular solution model (marked by the dashed line).

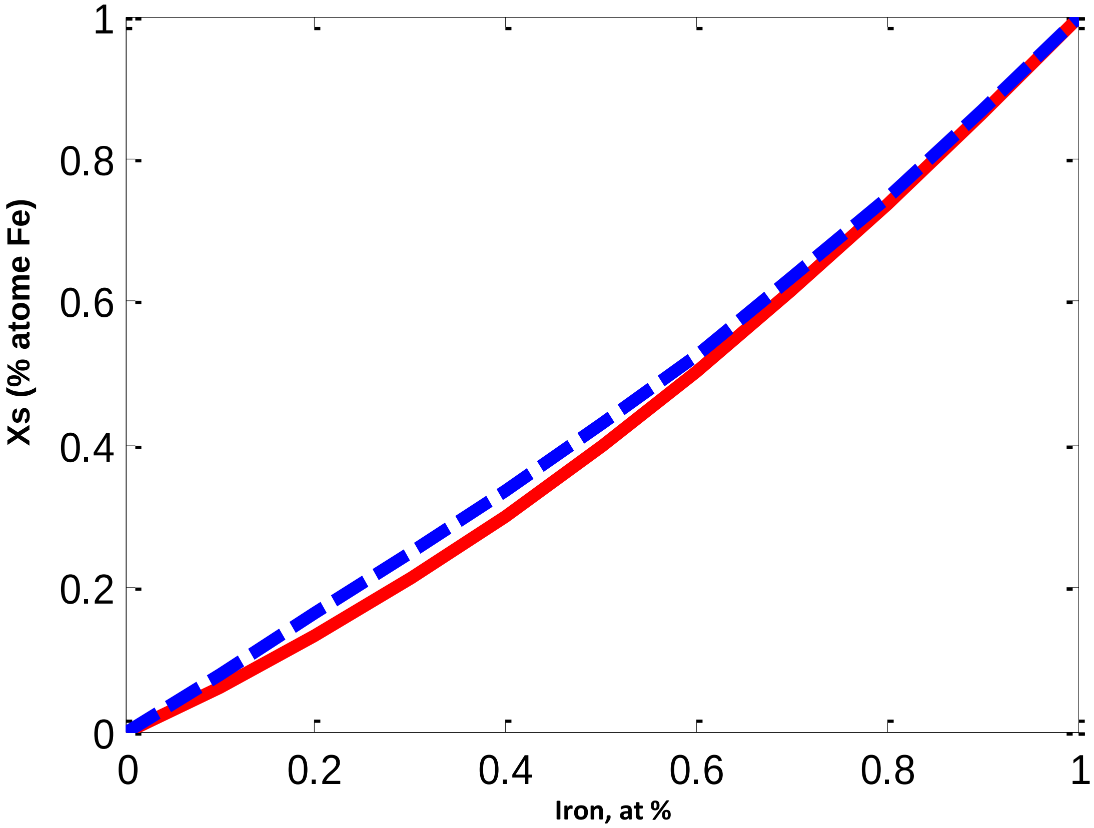

Fig.II.5: Variation of the surface molar fractions of Fe as a function of its bulk molar fraction for Cu-Ni system at T= 1546.15 K.

Figure II.5 shows that Ni will segregate at the surface of Fe-Ni in opposite of the Cu-Ni system. Ni is the surfactant element and it has a tendency to segregate at the surface ($\sigma_{Ni}^{l} < \sigma_{Fe}^{l}$, table II.1), but its segregation is week since the surface liquid tensions of pure Fe and Ni are closely. This segregation increased from X_{Ni}=100% to X_{Ni}=60% and decreased from X_{Ni}=60% to X_{Ni}=0% (pure Fe).

Comparing the results gives by the two considered models, we remark that the miscibility energy of Fe-Ni gives a weak contribution compared to the ideal case, which implies that the effect of the surface tensions is more predominant.

Figure (II.6) shows the variation of surface tension of Fe-Ni liquid alloys at 1546.15 K are plotted as a function of the Fe content for the ideal solution (solid line) and regular solution (the dashed line).

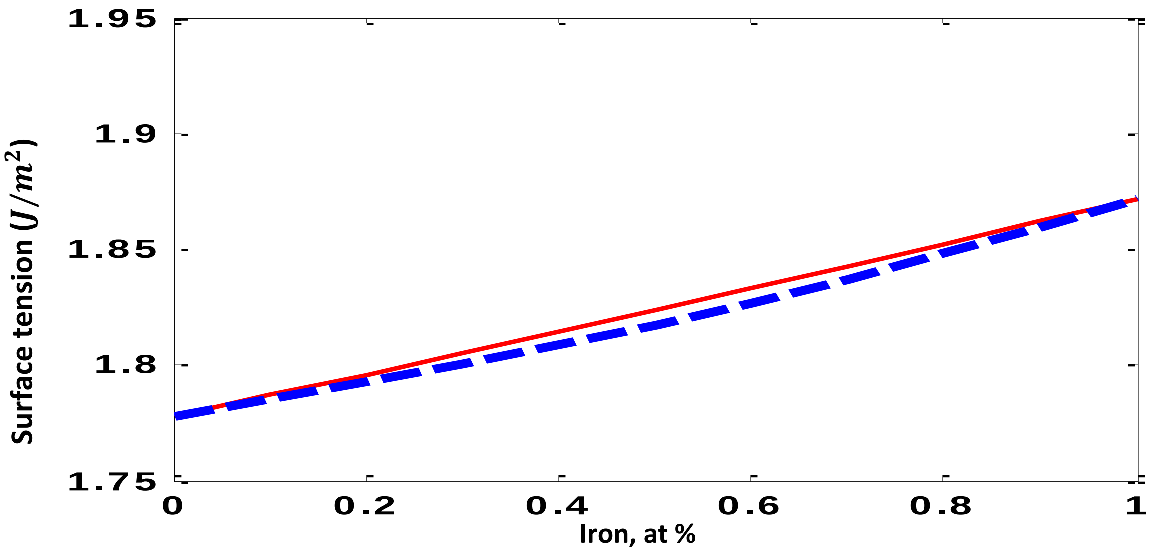

FIG.II.6: the variation of surface tension of liquid system Fe-Ni as a function

of its bulk molar Fraction at T=1546.15K.

In Figure (II.6) we observe in both of models approximately a linear behaviour of surface tension with Fe composition. The small difference between the surfaces tensions of two models is due to the weak effect of Fe-Ni miscibility energy.

The comparison of surface tension the calculated and experimental [2] of the Fe-Ni system is shown in Figure (II.7).

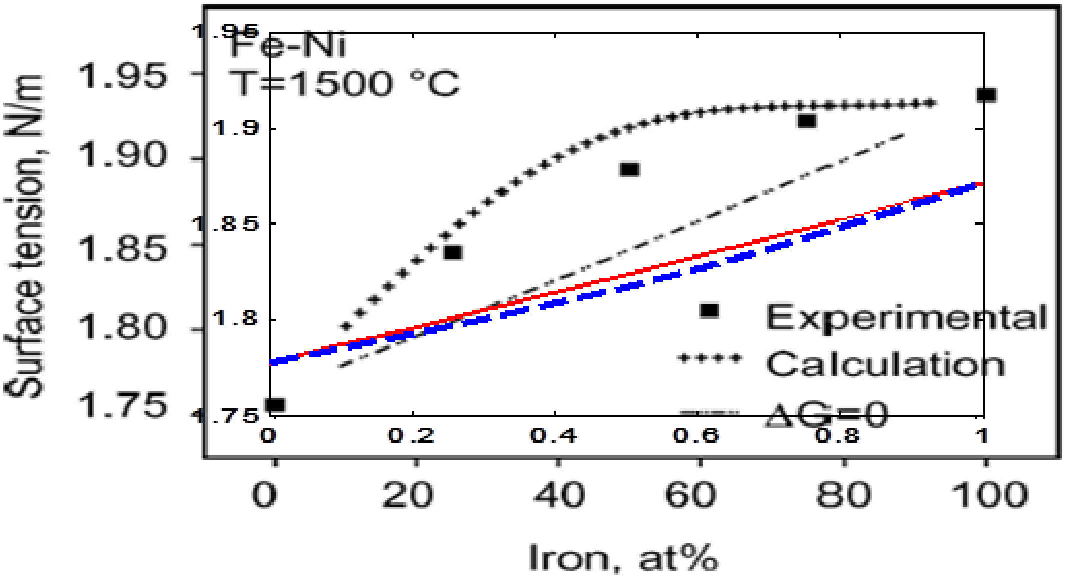

Fig.II.7: Comparison between surface tension of the calculated and

The experimental[2] of the Fe-Ni system.

We remark that our calculated curves and the calculated ones by [2] have a similar linear behaviour. The difference between values is due to the fact that in our model we didn't take in account the variation of the liquid surface tension with temperature and our model is a simple model which is so far to reach the real situation.

II.5.3. Calcul des tensions de surface du système Al-Ni

For this system, since Al is not a transition metal, we use another formula to calculate the miscibility energy in Al-Ni system (equation II.7). We calculate the molar fraction of surface of Ni as a function of the molar fraction in bulk (from 0 to 100%) at T = 1673 K (This temperature was chosen according to the experimental work in []) Equations using in calculations of the surface segregation and the surface tension in Fe-Ni are the same for the Cu-Ni system (equations II.20 and II.26).

Figure (II.8) shows the variation of the molar fractions at surface of the liquid phase as a function of the molar fractions in bulk volume of the liquid for the ideal solution (solid line) and regular solution (the dashed line).

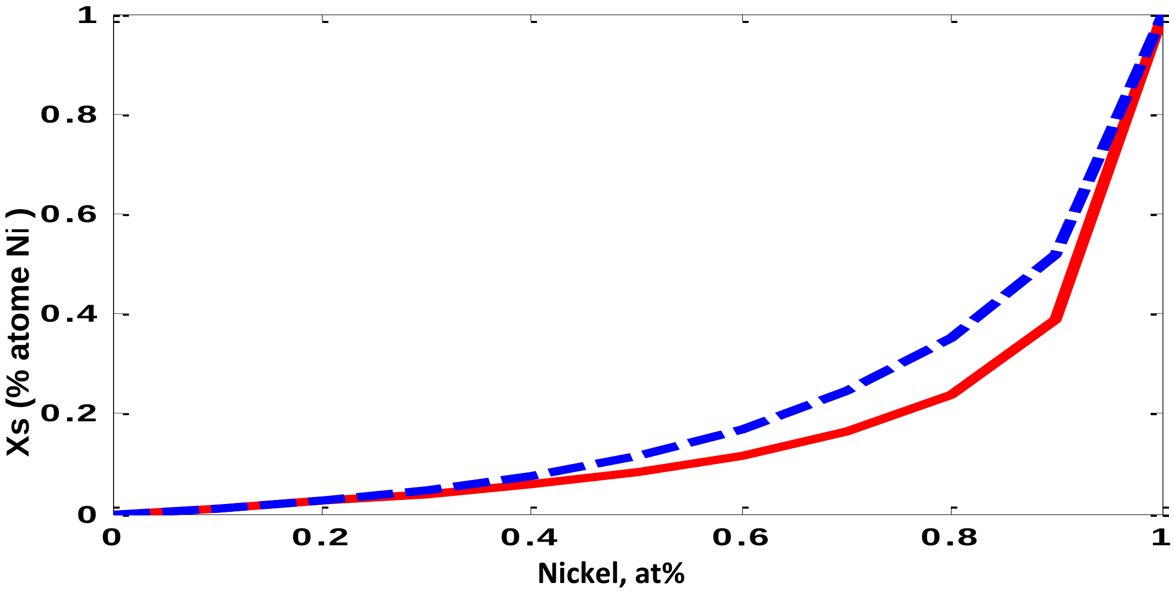

FIG.II.8: The variation of surface tension of liquid system Al-Ni of its bulk molar

fraction at T=1673K.

Figure (II.9) shows the variation of surface tension of Al-Ni liquid alloys at 1673 K are plotted as a function of the Ni content for the ideal solution (solid line) and regular solution (the dashed line).

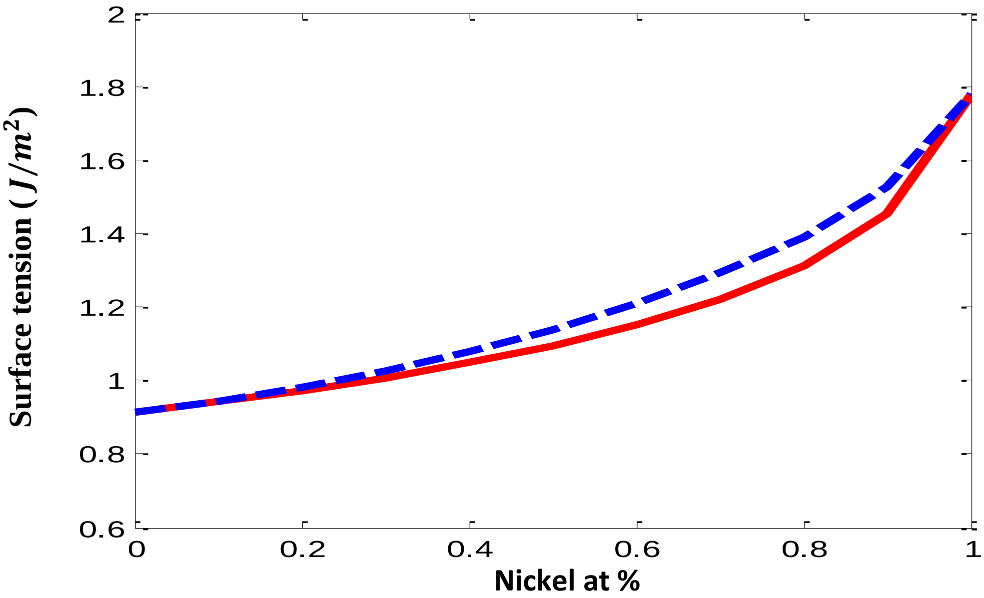

Fig.II.9: the variation of surface tension of liquid system Al-Ni of its bulk molar

Fraction at T=1673K.

In Figure (II.9) we observe in both of model a strong variation curve of surface tension with a composition between the surface tension limits for each component of pure metal in binary alloys. Ni surface tension increases sharply with increasing Fe content, and the small difference between the surfaces tensions of two models is due to the introduction of the miscibility energy which has a quit significant effect on the surface segregation of Al.

The comparison of surface tension the calculated and experimental [9] of the Al-Ni system is shown in Figure (II.10).

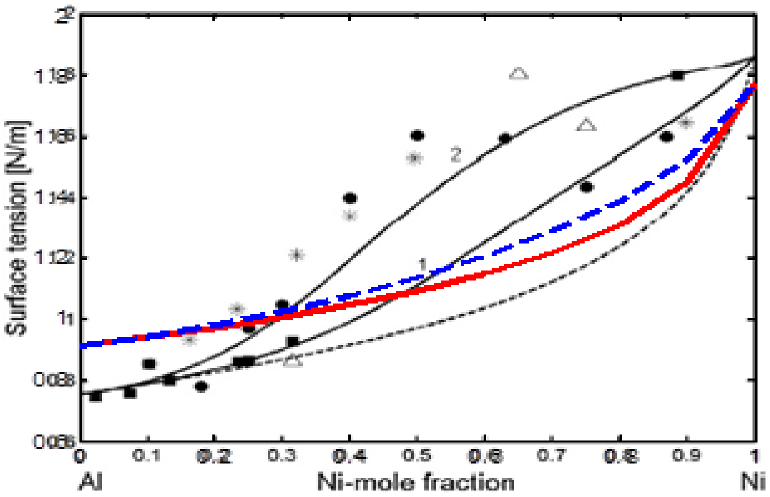

Fig.II.10: Comparison between surface tension of the calculated and experimental [9]of the Al Ni system at 1673 K.

Surface tension of liquid Al–Ni alloys at 1673 K (1 QCA model; 2 CFM model; ——— the ideal solution model)

Author of work [9] use three different models to calculate the surface tension:

- ✓ The QCA Model: the quasi-chemical approximation model
- ✓ The CFM model: the compound formation model
- ✓ The ideal solution model

Figure II-10 shows that our results are qualitatively agree with the ideal model of the work [9] but disagree with the others models. But the all models data and experimental values shows that study of surface tension of liquid Al-Ni is more complicated.

II.5.4. Calculation of surface tensions for system Fe-Cu

We calculate the molar fraction of surface of Fe as a function of the molar fraction of bulk (from 0 to 100%) at T = 1823,15 K

Figure (5) shows the variation of the molar fractions at surface of the liquid phase as a function of the molar fractions in bulk of the liquid for tow solution the ideal solution (solid line) and regular solution (the dashed line).

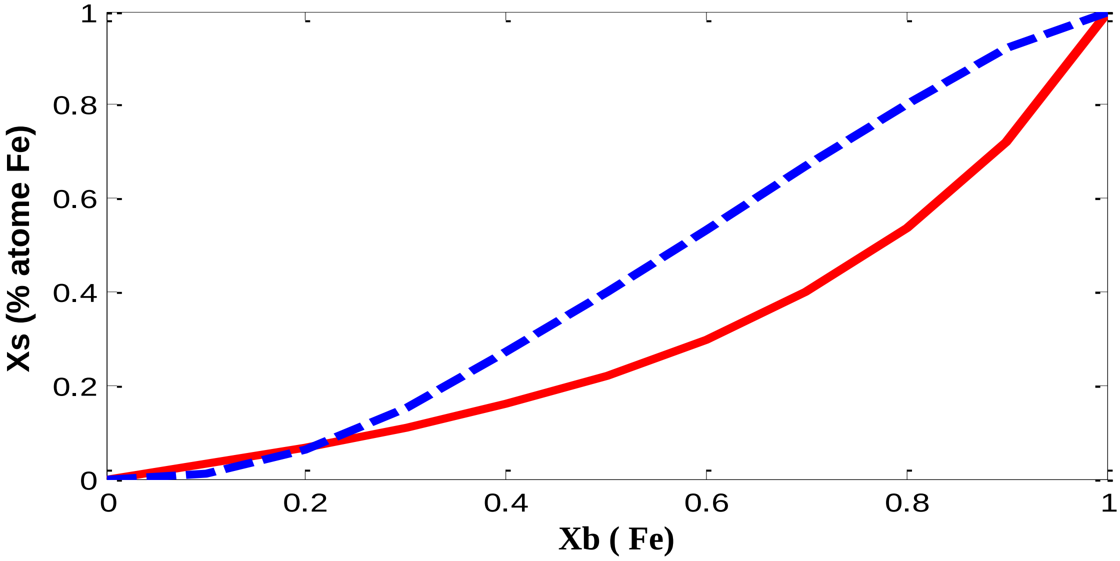

Fig .II.11: the variation of surface tension of liquid system Fe-Cu as a function of its bulk molar Fraction at T=1823,15 K .

Figure (II.12) shows the variation of surface tension of Fe-Cu liquid alloys at 1823,15 K are plotted as a function of the Ni content for the ideal solution the(solid line) and regular solution (the dashed line)

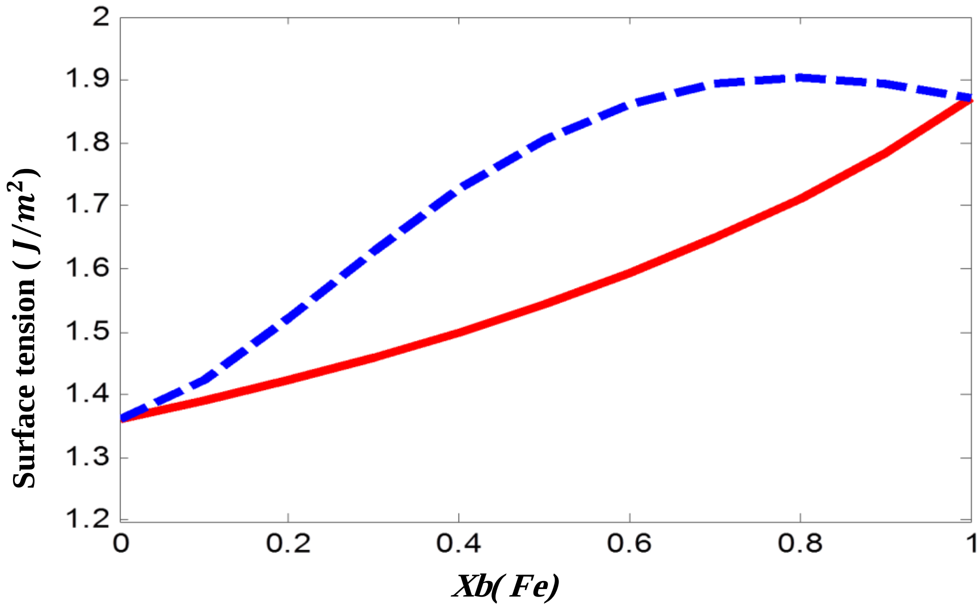

Fig.II.12: the variation of surface tension of liquid system Fe-Cu as a function of its bulk molar Fraction at T=1823, 15 K.

In figure (II.12) we observe in both models that the surface tension of Fe-Cu increase more slowly with increasing Fe content in the ideal case than in the regular solution model. The great difference between the surfaces tensions of two models is due to the introduction of the miscibility energy in a regular solution and the miscibility energy of system Fe-Cu is huge and negative value which is keeping the surface tension in regular solution high.

The comparison of surface tension the calculated and experimental [2] of the Fe-Cu system is shown in Figure II.13.

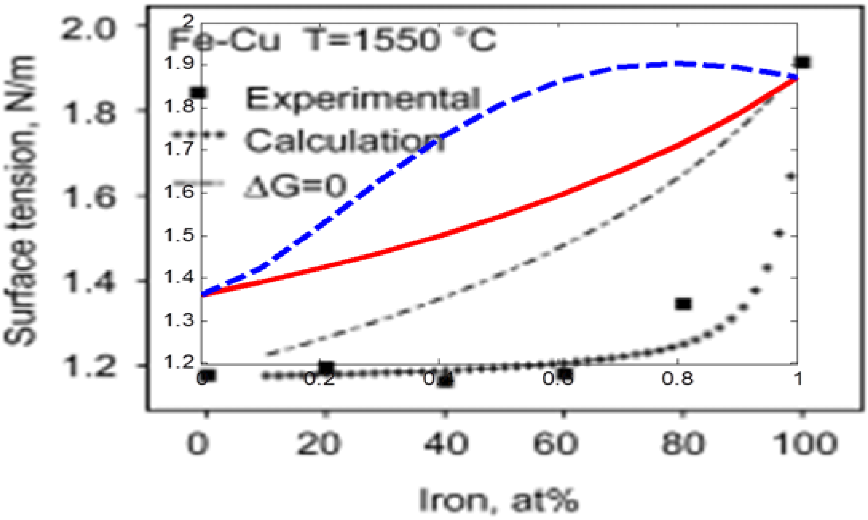

Fig.II.13: Comparison between surface tension of the calculate

and experimental [2]of the Al-Ni system

Curves in the ideal solution model are agreed qualitatively. But those of the regular solution model are completely in an opposite side.

General conclusion

General conclusion

After the calculations made in our work, we can conclude the following:

- Calculations of surface tensions were carried out on proven theoretical foundations.
- The surface tensions of the different phases of the Cu-Ni and Fe-Cu, Fe-Ni and Al-Ni systems were calculated in the equilibrium conditions.
- Calculation of the surface tensions requires the knowledge beforehand of certain physical properties of the components in their pure state, and also of the miscibility energies values of the solution in bulk and at the surface.
- The small difference in the results between the surfaces tensions in the two solution models (regular and ideal) is due to the weak effect of the miscibility energy.
- Our results are in general with a good qualitatively agreement with other more complicated models and the experience.

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Abstract

الملخص :

الهدف من هذا العمل هو حساب التوتر السطحي وتركيز السطح لأنظمة ثنائية بدلالة تركيز الحجم عند درجة حرارة ثابتة. وذلك استناداً إلى أسس نظرية مثبتة التي تربط التوتر السطحي بالخصائص الديناميكية الحرارية السائبة, هذا الحساب يطبق على أربعة من الانظمة الثنائية Ni-Cu وFe-Cu و Fe-Ni, Al-Ni باستعمال برنامج Matlab .

الكلمات المفتاحية :

الديناميكية الحرارية,التوتر السطحي , الانعزال السطحي , السبائك السائلة, المعادن الانتقالية

Abstract

The objective of this work is to calculate surface tension and surface concentration of binary systems on function of the volume concentration at a constant temperature .Based on proven theoretical foundations, which relates the surface tension to bulk thermodynamic properties. An application is made on five binary systems Calculations are established under MatLab environment.

Keywords: Thermodynamics, surface tension, surface segregation , liquid alloys, transition metals.

Résumé

L’objectif de ce travail est de calculer surface tension Et la concentration en surface des systèmes binaires. Avec une fonction de concentration à température constante ¸ En se basant sur des fondements théoriques avérés, qui relie la tension superficielle aux propriétés thermodynamiques globales .Une application est faite sur cinq systèmes binaires les calculs sont établis sous environnement MatLab.

Mots clefs : Thermodynamique, tension superficielle, ségrégation superficielle, alliages liquides, métaux de transition