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Surface Tension and Beyond: Physics of Liquid Interfaces

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Abstract: *Surface tension is a fundamental property of liquids, arising from the differences in intermolecular forces acting on surface molecules compared to those in the liquid's interior. This research explores the significance of surface tension, various measurement techniques, methods for reducing surface tension, and the adsorption of particles at surfaces to stabilize emulsions. It also examines the influence of Gibbs free energy on surface tension and the relationship between density gradient theory and interfacial tension.*

Keywords*:* Gibbs free energy, Density gradients, surfactant and Meniscus.

I. INTRODUCTION

To attain an understanding of surface tension and its significance in our day-to-day lives as well as in several industrial applications, it is important to note that the use of interfacial tension qualities occurs whenever one is doing actions such as washing clothes or painting a wall [1-11]. Insects walking on water or water droplets making perfect spheres are also examples of this phenomenon. There are also interfaces between liquids and gases, liquids and liquids, and solids and liquids. A liquid's surface tension is the cohesive force that acts at the surface of the liquid, causing it to behave in a manner similar to that of a thin membrane that has been stretched. A cohesive force at the surface results from the attraction between similar molecules. Because there are fewer neighboring molecules at the surface, an imbalance in these forces occurs. These forces are often referred to as intermolecular forces or van der Waals forces. Surface molecules are unstable due to unequal attractive forces, which tend to drive them away. Consequently, the liquid seeks to minimize its surface area until equilibrium is reached. One method for measuring surface and interfacial tension is force tensiometry, which encompasses techniques such as the Du Noüy ring method and the Wilhelmy plate method. The optical tensiometry technique, which analyzes the shape of a drop, is similar to the pendant drop method. Both methods evaluate the force exerted on a probe at the interface.The capillary rise method, bubble pressure method, drop-weight method, and spinning drop method are additional common techniques for measuring surface and interfacial tension. The spinning drop method is especially effective for measuring very low interfacial tension.

By incorporating surfactants such as soap or detergent, along with addressing insoluble contaminants like oil or grease and increasing the liquid's temperature, we can effectively reduce its surface tension through specific reduction methods. Surfactants and impurities work to disrupt the forces at the surface, which decreases the overall cohesive force and promotes the dispersion of the liquid. Surfactants are categorized into four primary types based on the charge of their hydrophilic (water-loving) head groups: amphoteric (which can carry both positive and negative charges depending on the pH), cationic (which carries a positive charge), non-ionic (which carries no charge), and anionic (which carries a negative charge). They are widely used and possess unique properties.An emulsion is a mixture of two liquids that do not mix, with one liquid dispersed as droplets within the other. This process requires energy input and the use of emulsifiers for stabilization. Emulsifiers, which are similar to surfactants, create a protective barrier at the interface of the two liquids. This barrier helps prevent the droplets from merging, thus stabilizing the emulsion. They achieve this by forming rigid interfacial coatings and increasing either electrostatic or steric repulsion between the droplets. Emulsions are widely used in various sectors, including food, cosmetics, and petroleum. An emulsion is a thermodynamically unstable mixture of two immiscible liquids, where one liquid is dispersed as droplets within the other. The formation of an emulsion requires energy, such as agitation or homogenization, to overcome the natural tendency of the liquids to separate. Emulsions are stabilized by emulsifiers, which are molecules that reduce interfacial tension and create electrostatic (long-range) or steric (short-range) repulsion between the dispersed droplets, utilizing either electrostatic or steric effects.

2.1 Molecular expansion of liquid

At the molecular level, surface tension results from imbalanced intermolecular attractive interactions among liquid molecules, rather than from molecular expansion. [8-11] Molecules in the bulk of the liquid are surrounded and experience balanced forces, while those at the surface are pulled inward, reducing the surface area to the smallest possible extent. This inward force creates a "skin-like" layer on the surface that exhibits tension. In a bulk liquid, the net repulsive force from nearby molecules and the net attractive force from distant molecules are, on average, both zero. This balance leads to random thermal motion. Due to the decreased density in the surface layer, there are fewer extremely close neighbors to exert an outward repulsive force. Consequently, molecules at the surface experience an inwardly imbalanced force, leading them to accelerate inward. However, as these descending molecules encounter the upward repulsive forces from the inner molecules, this inward acceleration cannot extend into the bulk of the liquid. Stronger attractive forces exist between the surface molecules on the liquid side because there are fewer nearby molecules on the air side. The schematic representation of molecular expansion is given in fig 1a and molecular expansion with cohesive forces is shown in fig 1b. This phenomenon results in the observation of surface tension on the liquid's surface. Overall, the molecules at the surface being pulled inward lead to a reduction in the surface area. Because a sphere has the lowest surface area for a given volume, liquid droplets often form spheres. The bulk liquid molecule that is joined to its neighbors at the surface has more attractive bonds in terms of surface energy. In order to produce a new surface, some connections must be broken. This results in the creation of an electrostatic surface charge, which is the result of doing work and is known as surface free energy. It has to do with coating material qualities, where antifouling capabilities are linked to low surface energy. It has been demonstrated numerically that a liquid's potential energy is highest at its surface. It is equivalent to the surface energy numerically and is a scalar number. It is measured in dynes/cm and has the same dimensions as surface tension.

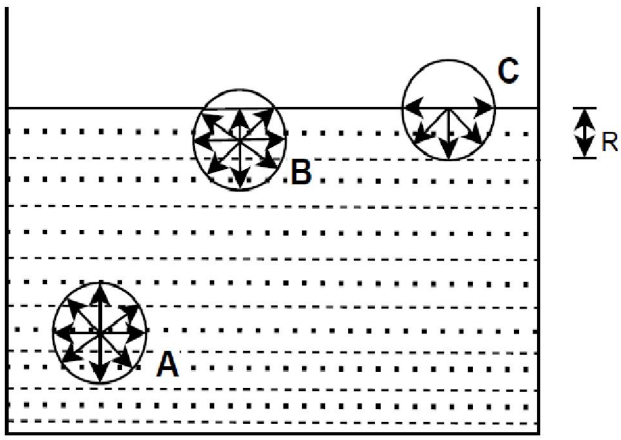

Fig 1a: Schematic representation of molecular expansion.

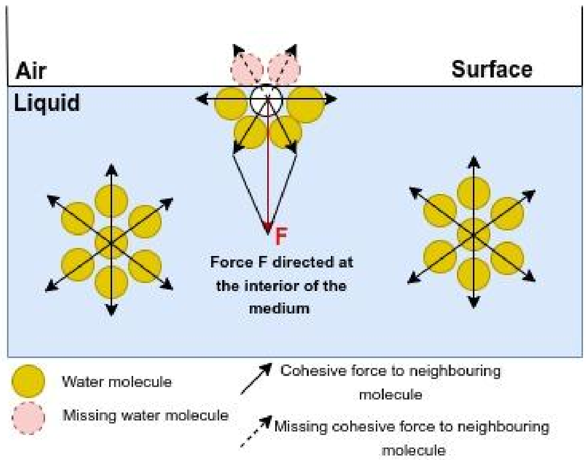

Fig 1b: Molecular expansion with cohesive forces.

The expansion of liquid due to temperature change is described by the formula:

$\Delta V = \beta V_0 \Delta T$,

Where ΔV is the change in volume, V_0 is the initial volume, ΔT is the change in temperature, and β is the coefficient of volumetric (or cubical) expansion. This formula indicates that the change in volume is directly proportional to the initial volume and the temperature differential. As liquids conform to the geometry of their container, only volumetric expansion can be directly quantified. Understanding this relationship is crucial in fields such as engineering and materials science, where precise measurements are necessary for designing systems that can withstand thermal fluctuations.

2.2 Gibbs energy and definition of the surface tension

We present a more effective equation for surface tension. We accomplish this in two stages. Initially, we aim to derive an equation for the variation in Gibbs free energy. [8-14] The Gibbs free energy G is typically more significant than F due to its natural variables, temperature (T) and pressure (P), are constant in most applications. Secondly, we know that, for curved surfaces, surface tension is not uniquely determined and depends on where precisely we choose to position the interface.

We express the Gibbs free energy as

$dG= -SdT+ V^{\alpha} dP^{\alpha}+ V^{\beta} dP^{\beta}+\sum \mu_i dN_i+ \gamma dA$

Assuming that the interface is flat (planar) we have the same pressure in both phases and we get

$dG= -SdT+ VdP+\sum \mu_i dN_i+ \gamma dA$

With the help of this equation it is also possible to give a definition of the interfacial tension,

$\left(\frac{\partial G}{\partial A}\right)_{T,P,N_i}=\gamma_i$

The surface tension is the increase in the Gibbs free energy per increase in surface area atconstant T, P, and N_i .

2.3 Density gradient theory:

The interfacial tension can be easily determined by density gradient theory with a suitable combination of an equation of state. The formula used is: [6-9]

$$\sigma = \int_{-\infty}^{+\infty} \sum_{i=1}^{N} \sum_{j=1}^{N} v_{ij} \frac{d\rho_i}{dz} \frac{d\rho_j}{dz} dz$$

Here, $i = 1 \dots N.$ thevalues of the pure component influence parameter are obtained by fitting with experimentally measured interfacial tension at fixed temperatures. Here,the density distributions across the planar interface are $d\rho_i$and $d\rho_j$.

3.1 Factors that affect the surface tension of liquids:

3.1.1 Temperature: -As the temperature of a liquid rises, its surface tension diminishes to its lowest point. This occurs because increased temperature enhances molecular thermal activity, thereby elevating the kinetic energy of the molecules, [8-14]

which weakens the cohesive forces among them. Consequently, the intermolecular cohesive force decreases, leading to a reduction in surface tension. Elevated water temperatures decrease the surface tension of soap solutions. This facilitates the soap's dispersion and infiltration into materials, enhancing the efficacy of the cleaning process. The relationship is essential in several applications, including cleaning and other liquid-related activities.

3.1.2 Surfactant: -The purpose of a surfactant is to lower the surface tension of a liquid. [8-14] Because of the strong molecular attraction, water has a high surface tension. The molecules of surfactants are weakly attracted to one another. Some of the surfactant molecules go to the water's surface when it is introduced to a liquid, such as water. As a result, the water/surfactant compound's surface develops a layer of molecules that are weakly attracted to one another, improving the water's ability to wet surfaces. Surfactants facilitate the mixing and formation of stable emulsions by lowering the interfacial tension between water and oil.

3.1.3 Impurities: -The introduction of impurities into a liquid can disrupt cohesive forces, resulting in an increase or decrease in surface tension, contingent upon the characteristics of the impurity. [8-14]The dissolution of organic substances in water results in a reduction in water's surface tension due to a drop in intermolecular forces, as observed with substances such as soap, phenol, and toothpaste. The dissolution of an inorganic material, such as salts, in water

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results in a rise in the surface tension of water due to the enhancement of intermolecular forces when the inorganic substance dissociates into ions. Insoluble contaminants, such as dirt, oil, or grease, diminish the surface quality.

3.1.4 Oxidation: -Surface tension is directly impacted by oxidation. A variety of compounds' surface tension is reduced by atmospheric oxygen. [8-14]Oxygen-rich oxide layers reduce surface tension by changing the atomic makeup and interactions at the surface, just like liquid metals do. The presence of oxygen causes an oxide layer to grow on molten metals, such as alloys based on gallium and aluminum, which considerably lowers surface tension. This is because the metallic bonds that contribute to surface tension can be weakened by oxygen atoms physisorbing or chemisorbing onto the metal surface. As demonstrated by some liquid gallium-based alloys, on the other hand, the development of an asymmetric oxide skin can cause some oxidized surfaces to have a greater effective surface tension.

3.1.5Interfacial Tension: -A liquid interface is a phase boundary between two phases, one of which is liquid. Interfaces may be either flat or curved based on the neighboring phases. [8-14] The categorization of interfaces is as follows: Liquid-gas interface, liquid-liquid interface, and solid-liquid interface as shown in fig 2a and expansion of liquid film when force F applied is given in fig 2b. Interfacial tension is the Gibbs free energy per unit area of the contact under constant temperature and pressure. Interfacial tension arises when a molecule at an interface experiences distinct molecular interactions compared to an analogous molecule within the bulk fluid. Interfacial or surface tension occurs in the presence of two distinct phases. These phases might be gas/oil, oil/water, or gas/water and are often measured in dynes/cm. The surface tensions for some liquids at a given temperature are given in a table 1.

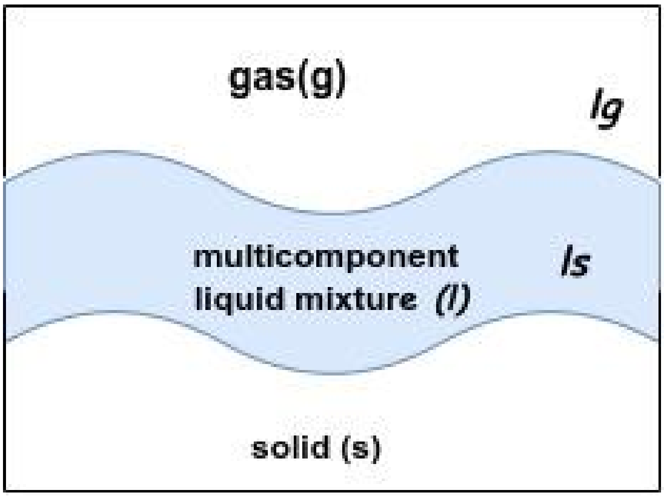

Fig 2a: Solid-Liquid-Gas interfaces.

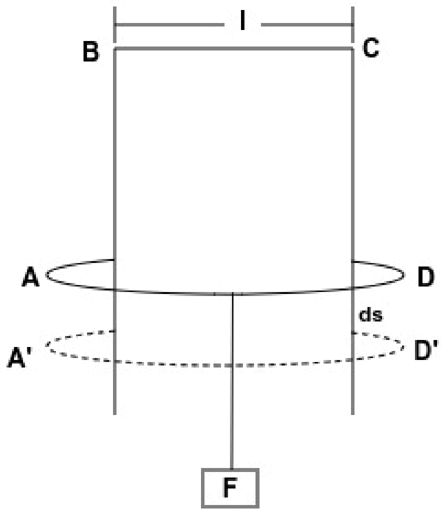

Fig 2b: A film of liquid being expanded with a force F.

Table 1: Surface tensions for some liquids at a given temperature are given below: [4,5].

S.No	Liquid	Temperature (C)	Surface Tension (γ)
1.	Benzene	20	28.88
2.	Heptane	20	20.14
3.	Water	25	71.97
4.	Ethanol	20	22.27
5.	Sodium Chloride	20	114
6.	Mercury	20	486.5
7.	Blood	22	55.89

Surface tension of Liquid in dyn/cm against air is equivalent to the SI unit of mN/m.

3.2 Surface tension related to nature

We can find number of examples where surface tension plays a vital role in our life [6-8]:

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3.2.1 Capillary Action: Capillary action refers to a liquid's capacity to ascend in confined regions independent of gravitational influence. The smaller the tube, the higher the water level must rise to equilibrate the adhesive force. The mathematical formula for the height (h) of a liquid column is: $-h = \frac{2T}{\rho rg}$

Where T= surface tension, r = radius of the tube, g = 9.8 ms^{-1} and ρ = density of the liquid.

This phenomenon should be observed with the liquid molecules present between the bristles of a paintbrush, within a narrow tube, in porous substances like paper, in some non-porous materials (such as liquefied carbon fiber), or within a biological cell.

3.2.2 Insects Walking on Water: Water striders are one example of an insect that can float on water's surface. In order to prevent the water strider from sinking due to gravity, the water's surface tension acts as a enough barrier. In order to make the most of surface tension, their legs have evolved to spread their weight across a wider region. Adhesion describes the force between two dissimilar things, like glass and water, while cohesion describes the force between two similar substances.

3.2.3 Soap Bubbles: Soap decreases the surface tension of water, facilitating the formation of bubbles. Soaps and detergents are intricate compounds that function in a certain manner. Water molecules exhibit cohesion due to intermolecular forces. Soaps and detergents facilitate cleaning by reducing the surface tension of water, enabling more liquid penetration into pores and soiled regions. The soap comprises elongated chains of carbon and hydrogen atoms linked with ionic compounds. The surface tension forms a delicate layer that maintains the bubble's shape.

3.2.4Washing with Hot Water: - Hot water may provide a similar effect. Elevated water temperatures decrease the surface tension of soap solutions. This facilitates the soap's dispersion and infiltration into materials, enhancing the efficacy of the cleaning process. The elevation in energy diminishes the intermolecular interactions that hold water in the ionic state when it is cold. Washing garments in hot water may not always be advisable due to potential damage; thus, always heed the care label instructions on the appropriate water temperature for laundering.

3.2.5 Drop of Liquid: While administering eye drops, we observe several occurrences of liquids splattering from a solid surface; similarly, raindrops retain a spherical form owing to surface tension. The cohesive forces between water molecules draw them into a configuration that reduces surface area. Gravity exerts a force that distorts this perfect shape into the almost round form seen. In the absence of such force, together with other forces, droplets of all liquids would assume a generally spherical form.

3.2.6 Meniscus Formation: Examine a mercury thermometer; you may observe that the liquid within the tube exhibits either a concave or convex surface. The curvature of the fluid column's surface in a tight tube arises from the interplay between cohesive forces, which contribute to surface tension, and adhesive forces acting onto the container's walls. The greater the attraction of adhesion to cohesion forces, the formation of a concave meniscus occurs, enabling the liquid to ascend the walls of the container between water and glass. If the intermolecular forces among the liquid particles exceed those between the liquid and the container material (e.g., mercury and glass), a convex meniscus is produced. Meniscus formation is extensively utilized in the calculations of contact angle and surface tension within the field of surface science.

3.2.7 Floating Objects:A needle or a paperclip can float on the water's surface if positioned gently, despite their greater density than water. Surface tension allows a needle or paperclip to float on the water's surface when put gently, despite its greater density than water. The surface tension forms a "skin" that sustains the object's weight. type of "membrane" that bears the object's weight.

3.2.8 Ink in a Fountain Pen: Fountain pens provide for smooth writing by drawing ink to the nib by capillary action, with the help of the ink's surface tension. These instances illustrate the critical function of surface tension in several everyday activities, both natural and artificial.

3.3 Applications of surface tension in daily life

The concept of surface tension is fundamental to many aspects of our everyday lives. In order to alter surface tension, several technological and chemical advancements have been made[6-12].

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Soaps and detergents serve several functions in daily life. All items are thoroughly cleansed when washed with soaps or detergents. The reduced surface tension of water facilitates the washing action of soaps and polymers. This facilitates the efficacy of soaps and detergents, allowing them to penetrate sections of garments or other items that are significantly soiled. The surface tension counteracts the interior pressure of the bubble.

The surface tension of water diminishes with an increase in temperature. The molecules of water begin to move immediately upon heating. The intermolecular attractive forces diminish, allowing the heated water to spread across a greater surface area.

Surface tension is significant in both physics and chemistry. The Hay's test is conducted for those with jaundice. This test is mostly founded on the characteristic of surface tension.

The capacity of a liquid to traverse tiny distances against gravitational forces is referred to as capillary action. The interaction between glass and water is attributed to a force known as adhesion. Surface tension causes the inside of the glass to compress and the liquid molecules between the bristles of a paintbrush to ascend.

On top of a mercury tube, the liquid is constantly either convex or concave. Surface tension between the cohesive and adhesive forces that exist between the tube's walls is the reason behind this. A meniscus is created in this manner. It is frequently used to compute surface tension and contact angles.

Water, alcohol, plus a few other sugars make up wine. Wine rises from the glass's sides as a result of the capillary action of the glass. The increased vapour pressure causes the alcohol to evaporate. Surface tension rises as a result. Droplets form on the wine's surface as a result.

For many everyday activities, surface and interfacial tension can be crucial. As a result, several substances and techniques have been created to alter surface and interfacial tensions.

IV. CONCLUSION

Liquid surface tension influences many processes and events. Many applications are possible in physics, chemistry, industry, technology, and daily life. Temperature, contaminants, surfactants, oxidation, and interfacial tension, among others, influence surface tension. All liquids have surface tension. Surface tension is caused by cohesive forces, which reduce a liquid's surface area and stretch it like a membrane. Strong molecular attraction from hydrogen bonding raises water surface tension. Two immiscible liquids spread as droplets inside each other form an emulsion, which requires energy and emulsifiers to stabilize. Emulsifiers, like surfactants, protect the interface from droplet coalescence and stabilize the emulsion. They create stiff interfacial coatings and increase droplet electrostatic or steric repulsion. Scientists and engineers are creating new ways to make life easier. We use it to improve medicine, cleaning, and cosmetics.

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