

## Introduction to surface tension

The interface between a liquid and its adjoining material (may it be another liquid, a solid, or a gas) is naturally under a mechanical state of tension. It is as if the liquid interface wants to shrink in area, but is held stretched by some forces (just like the rim of a trampoline holds the trampoline sheet in a stretched state). This property of a liquid interface is called **SURFACE TENSION** (see figure 1).

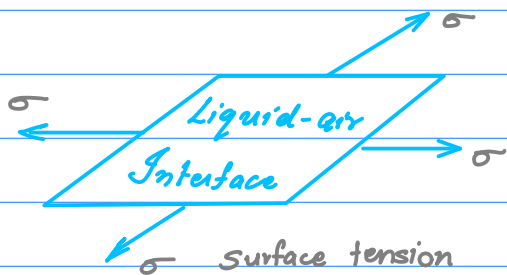
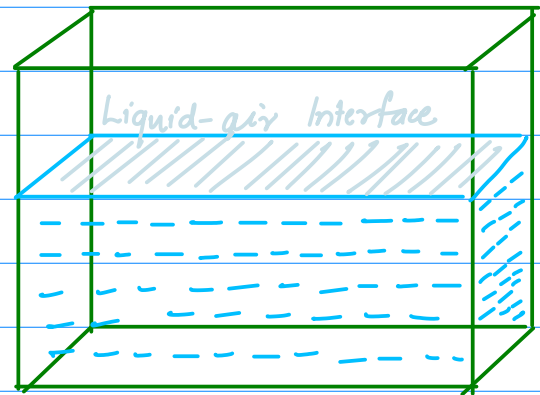


Figure 1



Mechanically, surface tension is represented by an internal force per unit length acting along the interface. By an internal force, we mean a force exerted by one part of the interface on another. For a free body diagram for a portion of the interface, we need the force exerted by the neighboring fluid interface.

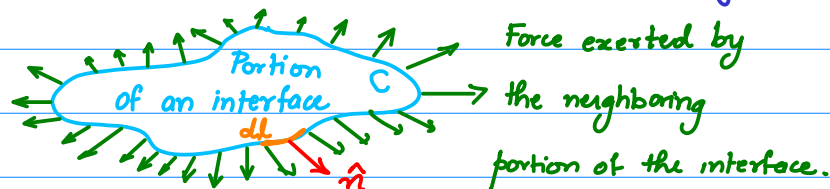


Figure 2.

For a liquid interface, the net force exerted by the neighboring portion of the interface  $\underline{F}$  may be written as

$$\underline{F} = \int_C \sigma \hat{n} dl \quad (\text{see figure 2})$$

- infinitesimal line element
- unit normal to the curve  $C$ , but tangent to the interface
- Coefficient of surface tension A-K-A. surface tension A-K-A interfacial tension.
- Curve describing the boundary of the portion

## Molecular origin of surface tension

The reason underlying the presence of surface tension on liquid interfaces may be traced back to the reason underlying the existence of the liquid state itself. In this section, we explore the thermodynamic origin of surface tension. The chain of reasoning justifying the claim is briefly presented below.

For more details refer to "Intermolecular and surface forces" by Israelachvili.

1. The liquid state exists due to a weak attractive force between the molecules of the liquid. In the absence of such an attractive force, the interaction between the molecules is limited to a short range repulsion, causing collision between the molecules, and leading to a gaseous state.



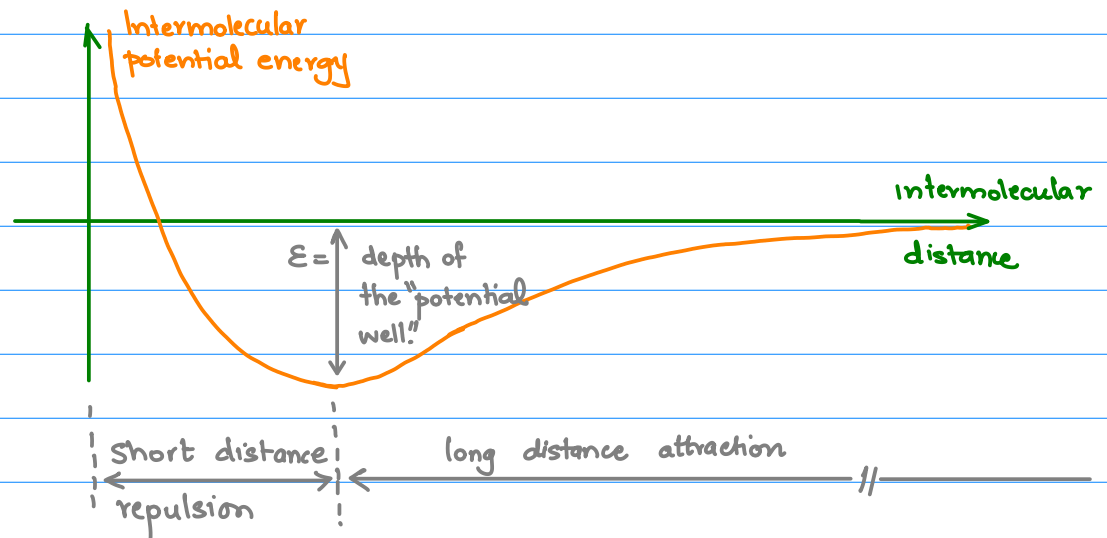
An assumption underlying the kinetic theory of gases is that attractive interaction between molecules be negligible (compared to their kinetic energy). In the absence of such an interaction, the molecules move more or less in a straight line between collisions and thus fill the whole volume available to them, which is the defining characteristic of a gas. Violation of this assumption causes a departure from gaseous state and underlies the formation of the liquid state.

2. A gas condenses when the average kinetic energy of the molecules becomes comparable to the attractive potential energy.



As the temperature of the gas is reduced, the kinetic energy of the molecules decreases (the kinetic energy is proportional to the temperature according to statistical mechanics). At the melting point, the kinetic energy is comparable to the intermolecular attractive potential energy.

3. The attractive interaction between molecules may be characterized by an intermolecular potential energy.



The depth of the potential well  $\epsilon$  characterizes the scale for the energy needed for molecules to escape from the attractive interaction. This energy is provided to the molecules in the form of random thermal kicks provided by the jiggling of the neighboring molecules. The magnitude of these kicks is characterized in terms of the average kinetic energy of the molecules, which is given in terms of the absolute temperature as  $k_B T$  ( $k_B$  = Boltzmann constant). When  $\epsilon \approx k_B T$ , molecules start to "coagulate" because the thermal jiggling is not enough to break the attractive bond between the molecules. This is how a gas condenses, typically into a liquid state for small molecules like water.

Thus an order of magnitude estimate for the interparticle attractive potential well  $\epsilon \approx k_B T_m$ , where  $T_m$  is the melting temperature.

$$\text{For water } T_m = 100^\circ\text{C} = 373\text{ K.} \Rightarrow \epsilon \approx k_B T_m = (1.38 \times 10^{-23} \text{ J/K}) (373 \text{ K}) \\ \approx 5 \times 10^{-21} \text{ J}$$

For liquid Helium,  $T_m \approx 4\text{K} \Rightarrow \epsilon \approx k_B T_m = (1.3 \times 10^{-23} \text{J/K})(4\text{K})$   
 $\approx 6 \times 10^{-23} \text{J}.$

4. Thus the energy of each molecule is reduced by an amount  $Z\epsilon$ , where  $Z$  is the average number of neighbors the molecule experiences. A typical  $Z$  is about 8 (see figure 3).

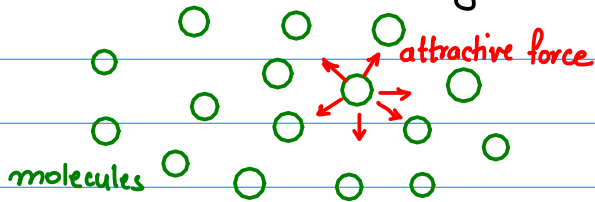


Figure 3. On average, the net attractive force balances out.

But what has all this got to do with surface tension?  
 Hang on, we are getting there.

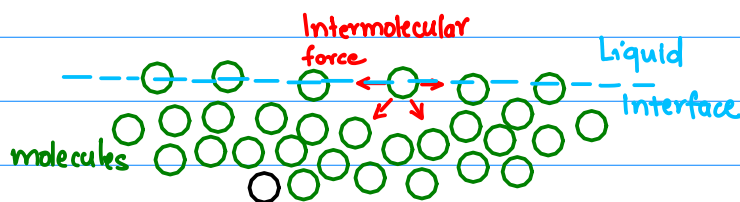


Figure 4.

At an interface, the molecules are missing a few neighbors (about half of them). These molecules have a higher energy due to the reduced number of neighbors. Thus there is excess energy associated with the molecules on the interface (see figure 4).

The magnitude of this excess energy may be estimated as:

Excess surface energy  $\approx \frac{Z\epsilon}{2\pi a^2}$ , where  $a$  is a typical molecular radius.  
 per unit area  $a \approx 1 \text{ nm}$  for small molecules like water.

Excess surface energy estimate:  $\epsilon_A$

For water:  $\frac{Z\epsilon}{2\pi a^2} \approx \frac{8}{2} \frac{5 \times 10^{-21} \text{J}}{3.14 \times (10^{-9} \text{m})^2} \approx 6 \times 10^{-3} \frac{\text{J}}{\text{m}^2}$

For Helium:  $\frac{Z\epsilon}{2\pi a^2} \approx 7 \times 10^{-5} \text{J/m}^2.$

The excess surface energy is closely related to surface tension.

5. Excess energy means lower density of molecules at the interface



The molecules on the interface are attracted towards the interior of the liquid. Think of either the unbalanced force or the excess surface energy for being on the interface. It is energetically not preferable for the molecules to be at the interface. As a result of this attraction, the density of molecules on the interface is less than that in the bulk. (schematically shown in figure 4.)

6. Lower density means larger average distance between molecules. Larger distance means excess attractive intermolecular force between molecules on the interface. Excess attractive intermolecular force means the presence of a SURFACE TENSION!

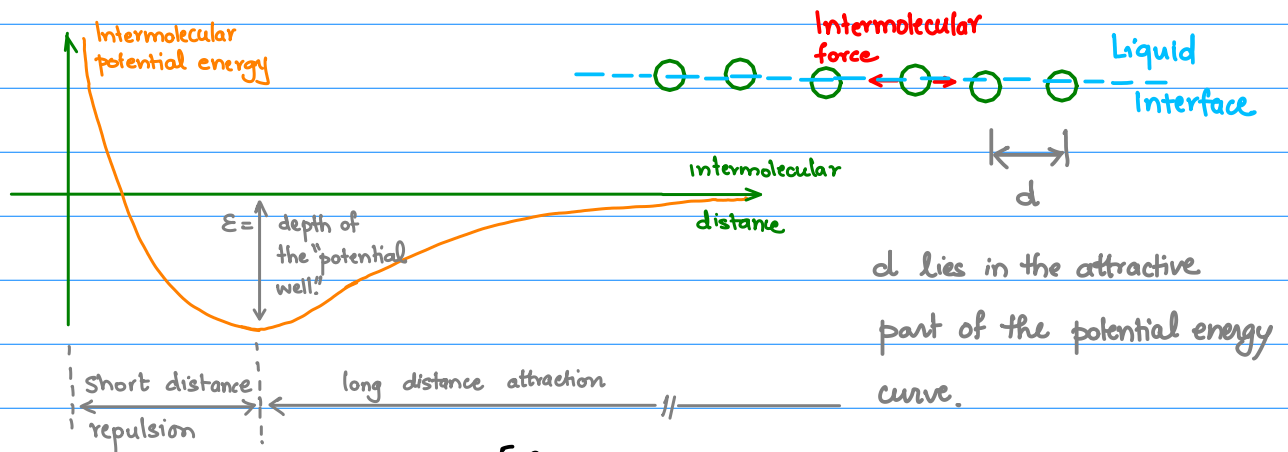


FIGURE 5.

HENCE, ATTRACTIVE INTERMOLECULAR FORCE LEADS BOTH TO THE EXISTENCE OF A LIQUID STATE AND THE SURFACE TENSION ON THE INTERFACE.

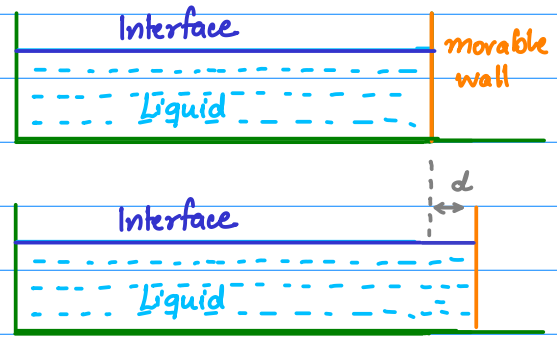
BUT WE CAN DO ONE BETTER. WE CAN ESTIMATE THE MAGNITUDE OF THE SURFACE TENSION.

There is a closer relation between the excess surface energy and surface tension.

Consider the thought experiment:

A trough with a movable wall filled with a liquid is shown in figure 6.

Imagine a situation in zero gravity.



The trough has width  $w$  in the direction perpendicular to the plane of

paper. By the way we defined the surface tension, the movable wall

experiences a force  $\sigma w$  due to the presence of the liquid interface.

Figure 6. A thought experiment.

Now imagine moving the wall a distance  $d$ .

- The area of the interface increases by an amount  $w d$ . Hence the excess interface energy increases by  $\epsilon_A w d$ .
- The work done by the the force moving the wall  $(\sigma w) \cdot d$ .

By the law of conservation of energy, the work done must all go into increasing the excess surface energy, because there is no other mechanism for the energy to be stored.



Think about it. Are there other components of energy I am ignoring?


As a result

$$\sigma w d = \epsilon_A w d \Rightarrow$$

$$\sigma = \epsilon_A$$

i.e. the excess surface energy is numerically equal to the surface tension

The units of the two quantities are also identical.

	$\sigma$ Force / length N / m	$\epsilon_A$ Energy / Area J / m <sup>2</sup>	But $J = Nm$ , hence the two units are identical.
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We made estimates of the excess surface energy. How do they compare with measured values of surface tension?

	Estimated	Measured	} We estimated surface tension within an order of magnitude. Especially with very approx. value of lengths and areas.
Water	$6 \times 10^{-3} \text{ J/m}^2$	$70 \times 10^{-3} \text{ N/m}$	
Helium	$7 \times 10^5 \text{ J/m}^2$	$3 \times 10^{-4} \text{ N/m}$	

This is awesome!

### Thermodynamic definition

Thermodynamically, surface tension is defined or identified in terms of an excess Gibb's energy  $G$  per unit area

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

That's it for the introduction to surface tension.