University *of Ljubljana*
Faculty *of Mathematics and Physics*

Seminar I_b - 1. year, II cycle

A basic macro- and microscopic view of surface tension and capillarity

author: Matjaž Zadnik

supervisor: prof. dr. Rudolf Podgornik

Ljubljana, November 2014

Abstract

Surface tension is a long known characteristic of liquids to make an interface. The microscopic interpretation of this mechanical force has just been better understood in the last decades, after the nature of intermolecular forces has been explained. Nowadays statistical physics together with thermodynamics and mechanics is indispensable for decent interpretation of capillary phenomena. In this seminar we will roughly examine from the microscopic point of view the origin of surface tension and of capillary forces near the contact line of different phases in liquids, where van der Waals interactions are predominant. We will also explain the connection between microscopic distribution of these forces and macroscopic quantities such as free energy and contact angle.

Contents

1 Introduction

Surface tension is a mechanical force which is mostly known to act along the liquid-vapour interface [1]. It has been been known long ago, that it is the cause of some curious phenomena in nature. For example, liquid drops won't spread on some surfaces, yet on the others will. Moreover, there is a force acting on a metal rod being pulled out of mercury bath and a pin floats on a water surface, but sinks when poked [1, 2]. While surface tension in liquids is a problem of its own, we are usually using a more general term capillary effects or capillarity when there are also solid interfaces involved.

Before scientists had enough insight into molecular structure of matter, the cause of surface tension in liquids and other capillary effects was quite a mystery. It was later found out that these effects indeed are a direct consequence of the nature of intermolecular forces and of thermal effects in an anisotropic molecular structure, so they are of direct molecular origin, even though they manifest on the macroscopic scale [1, 2]. Consequently, it was not until some decades ago, that these phenomena have been thoroughly researched. Nowadays, a good description of all mentioned phenomena involves macroscopic thermodynamics, fluid mechanics and statistical physics. However, many problems remain unsolved, especially the deviations from thermodynamic equilibrium [3]. Nevertheless, capillary effects have always been important in practical use: in textiles and clothing industry, dye industry, cosmetics, metallurgy, etc. [3].

First we shall describe the problem of surface tension in liquids. We will explain why is the surface tension a force parallel to the liquid-vapour interface. In the latter case we will limit ourselves to liquids, where intermolecular pair potential is composed of short range repulsion and long range attraction. Then we will also include solids and present some of the general properties of their wetting. We will show with an example the microscopic distribution of forces in liquid near contact line of liquid, vapour and solid phase.

2 Liquid-vapour interface

2.1 Thermodynamics - free energy of an interface

A system of bulk liquid and bulk vapour in thermodynamic equilibrium can coexist with a stable interface. Macroscopic quantities of interest can be approximated by van der Waals equation of state in both phases [2]:

$$p_0 = \frac{k_\mathrm{B}T}{v-b} - \frac{a}{v^2}\,, \tag{1}$$

where p_0 is the equilibrium pressure, T is the temperature and v is volume per molecule. The equation of state incorporates interaction between molecules with parameter b as excluded volume of a molecule representing repulsion and parameter a representing attraction. Pressure must be continuous on the both sides of the interface. In vapour second term on the right side in (1) can be neglected, while in liquid both terms are much greater than actual pressure, yet the pressure is still equal to their difference.

From the point of view of thermodynamics, surface tension γ_LV is introduced as an excess free energy per unit area A of an interface between liquid and vapour bulk phases [2]:

$$\gamma_\mathrm{LV} = \left(\frac{\partial F}{\partial A}\right)_{T,V,n}\,. \tag{2}$$

F is the whole free energy of a system of volume V containing n molecules at temperature T. In other words, γ_LV is the energy needed to increase the surface area by one unit, therefore its units are J/m^2 or N/m.

The excess free energy is due to anisotropic molecular structure near the interface [2]. For example, if we consider a liquid molecule in a vicinity of a liquid-vapour interface, we can see that its bonding with the neighbouring molecules is weaker in comparison with the bonding of a molecule in the bulk because of the missing neighbours in vapour (see figure 1). To create new interface though, some bonds must be broken and this involves the doing of work [4]. For start, we considered only crude microscopic picture based on the notion that liquid stays together [4]. We shall delve more into it later.

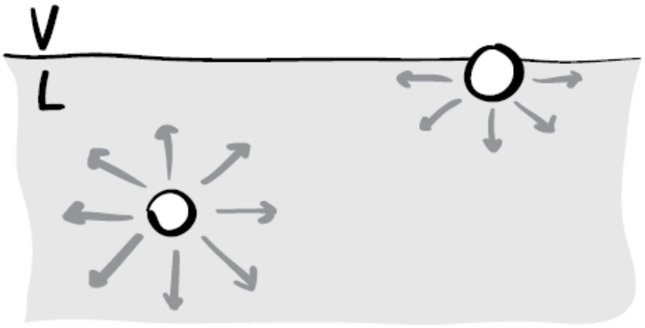


Figure 1: *Missing attractive bonds on a molecule at surface* [2].

The subscripted mark LV in (2) stands for liquid-vapour interface. By analogy with liquid, quantities of excess free energy of a surface can also be defined for solid-liquid (SL) and solid-vapour (SV) interfaces. They are also sometimes called solid-liquid and solid-vapour surface tensions [2].

Typical values of surface tension are of order [2]:

$$\gamma \sim \frac{\epsilon}{\sigma^2}\,, \tag{3}$$

where ϵ is a value of energy of molecular bond and σ is a typical molecular diameter. For oils with interaction strength $\epsilon \sim k_\mathrm{B}T$ the value is $\gamma_\mathrm{LV} \sim 0.02$ N/m [2]. In water hydrogen bonds increase the bonding energy, therefore $\gamma_\mathrm{LV} \sim 0.072$ N/m [2]. Even stronger are the bonds in mercury. They are of magnitude $\epsilon \sim 1$ eV, thus $\gamma_\mathrm{LV} \sim 0.5$ N/m [2].

2.2 Fluid mechanics - mechanical force

In the bulk liquid at equilibrium two neighbouring sub-parts of liquid act on each other with a force per unit area that is equal to the equilibrium pressure inside the liquid [2]. If the plane separating these two liquid subsystems crosses the liquid-vapour interface, an additional force between the subsystems must be added: surface tension (figure 2) [2]. Surface tension lies in a same plane as the liquid-vapour interface and is normal to the contour line, which is a line separating liquid subsystems at the interface (see figure 2). Contrarily to the pressure, surface tension corresponds to an attractive force [2]. It is proportional to the length of the contour line l.

The magnitude and direction of the surface tension can be easily derived with the help of thermodynamics through the virtual work principle [2]. Let us imagine that we slowly stretch the surface of a right liquid subsystem for $\mathrm{d}x$ in a direction normal to the contour line (figure 2). The surface area of the subsystem thus increases for $l \cdot \mathrm{d}x$ and all work done adds into free energy. Consequently, the increase of free energy is $dF = \gamma_{\mathrm{LV}} \cdot \mathrm{d}A = \gamma_{\mathrm{LV}} \cdot l \cdot \mathrm{d}x$ and is equal to the work of surface tension force. Therefore, the whole surface tension force is equal to $\gamma_{\mathrm{LV}} \cdot l$. From here it is obvious that the surface tension as energy per unit surface γ_{LV}, is numerically equal to the surface tension as force per unit length [2]. However, this is not true in case of solid-liquid and solid-vapour interfaces. Even though the two quantities have equal units and equal numerical value, we should be aware that they have different physical meaning [2].

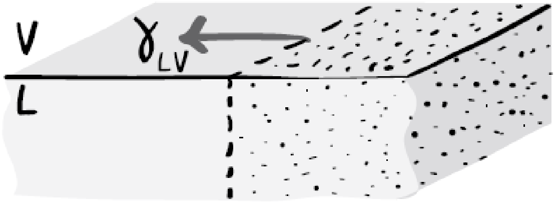


Figure 2: *Surface tension as a force per unit length* [2]. Force is exerted on the dotted subsystem by the gray subsystem, systems are divided by dashed line - the contour line. Surface tension is parallel to the interface and perpendicular to the contour line.

2.3 Microscopic picture

Matter is constructed from molecules. The molecular interactions in a liquid are mostly of two types. First there is a short range repulsion [2, 4] that originates from the repulsion of the electron clouds of the molecules, due to Pauli exclusion principle [2]. Secondly, there is long range attraction, which is caused by the dipole-dipole attraction or the so called van der Waals attraction [2]. Liquids, where this kind of interaction are dominant, are called van der Waals liquids. The mentioned type of intermolecular forces, especially in the case of spherical-like molecules, have successfully been modeled by Lennard-Jones pair potential (see figure 3) [1, 2, 5, 6]. One of its most popular variant is Lennard Jones 6-12 potential [5]:

$$\phi(r) = 4\epsilon\left(\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right). \tag{4}$$

Typical parameters of every Lennard-Jones type potential are typical interaction strength ϵ and effective molecular diameter σ. r is an intermolecular distance.

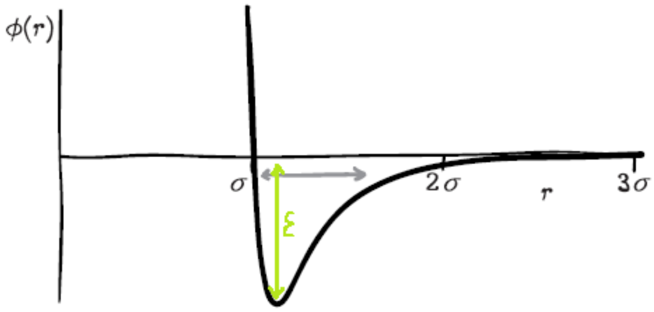


Figure 3: *Intermolecular potential* [2]. At distances $r < \sigma$ there is strong repulsion between molecules, but when $r > \sigma$ there is attraction. Grey arrow represent fluctuations of intermolecular distances due to thermal fluctuations, which is typical for liquids. Liquids are characterised by $\epsilon \sim k_\mathrm{B}T$. In solids, on the other hand, position of molecules is fixed $\epsilon \gg k_\mathrm{B}T$, yet in gas interactions are negligible $\epsilon \ll k_\mathrm{B}T$.

Molecules in a bulk liquid are free to move around. Motion is caused by heat and by forces from neighbouring molecules [2, 4]. In the bulk liquid both repulsive and attractive forces on a molecule are zero on average [4]. That's because the surroundings of a molecule is isotropic on average, but the resultant force is not zero at any instant.

However, the situation near surface is different. On average there is an unbalanced force on a molecule that points towards the bulk [4]. The reason lies in different nature of repulsive and attractive forces. Because of their short range, repulsive forces are considered as "contact forces" [2] and they scale directly with the density of molecules, which falls off rapidly and continuously near surface. Attractive forces on the other hand, fall off more slowly, so on average the resultant is nonzero [4]. Only a small fraction of molecules near surface have enough kinetic energy to break through the surface into vapour phase. An average net inward attraction only causes liquid to be compact and to have a stable interface with vapour [4]. One must not confuse that with the direction of the surface tension force [2, 4]!

In more complex systems Van der Waals forces are not the only cause of surface tension. In electrolytic solutions for example, surface tension is also caused by Coulomb interaction between ions [7]. Moreover, in metallic liquids (mercury) long range attraction is caused by metallic bonds and in water attraction is strengthened by hydrogen bonds [2].

3 Microscopic interpretation of surface tension

After we've cleared up our picture of liquid-vapour system with an interface, let us explain how the surface tension force arises. Figure 4 will be of much help. We will be considering stresses in liquid only up to ~ 10 molecular distances from liquid-vapour interface [2, 3]. Gravitational effects can thus be neglected. We will be interested in forces normal to the liquid-vapour interface and perpendicular to it. These forces per unit surface form diagonal elements of stress tensor p_N and p_T, the former represents stress normal to the interface and the latter tangential to it. We will examine this stresses **by considering the forces exerted on the dotted liquid subsystem by the rest of the liquid** (see figure 4).

The key will be in the different range of attractive and repulsive forces in liquid [2, 4], both tracing their origin to intermolecular interactions. The repulsive forces because of their short range are to a good approximation isotropic everywhere and scale with the density [2, 4]. They are less susceptible to molecular structure. The attractive ones, on the other hand, depend strongly the local structure because of their longer range. Thus they are strongly anisotropic near interface [2, 4] and isotropic only in the bulk.

First, we shall consider forces in a direction perpendicular to the interface. The repulsive forces increase with depth at first, but then saturate in the bulk. That's because density must change continuously from the vapour density to the bulk liquid density. System is in equilibrium, thus the attractive forces must balance the repulsive ones and the resultant is equal to external pressure: $p_\mathrm{N} = p_0$. The attractive forces then also increase with depth and saturate at bulk. The reason lies in the initial increase of the attractive volume and its effective density. Because of the limited interaction range, the further increase of the thickness of the grey liquid film above considered system does not have effect on attraction, which results in saturation.

Secondly, we consider forces parallel to the interface. Repulsion increases as we dive into the liquid (figure 4(b)) the same way as in the previous case (figure 4(a)). Yet attraction decays much more slowly as we move from bulk towards the interface in comparison with the previous case, as there is more liquid in the direction parallel to the interface than normal to it [2, 4]. Attractive forces near interface are thus strongly anisotropic. As a result, there is net attraction $p_\mathrm{T} = p_0 - p^t$ exerted by the left subsystem on the right one, which is the biggest at surface and then decays quickly towards bulk [2, 4]. Quantity p^t is the anisotropic part of tangential stress. To be clear, in the bulk attraction turns into repulsion that is equal to equilibrium pressure p_0 [4]. On figure 4 equilibrium pressure is left out, because it is much smaller than the stresses caused by surface tension.

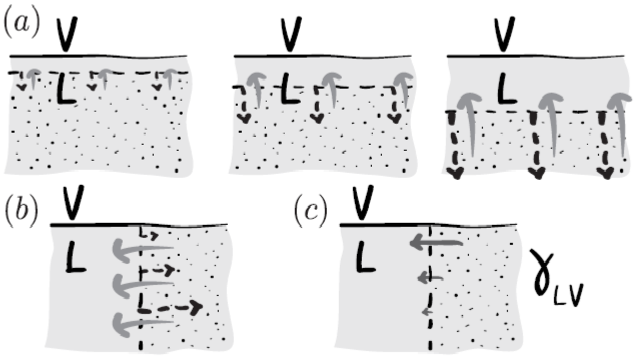


Figure 4: *Forces exerted on subsystem of liquid (depicted as gray and dotted) from the rest of the liquid (depicted as gray)* [2]. The subsystem is submitted to an attractive force (gray arrows) and a repulsive force (dashed black arrows). (a) The subsystem considered is the lower part of liquid and is separated from the rest with a dashed line parallel to the interface. (b) The liquid is now divided along a line perpendicular to the interface. As the repulsive forces are isotropic, they are of the same magnitude as in (a). Attractive forces decay more slowly as the repulsive ones. (c) This leads to a net attractive force from one side to the other.

Surface tension can be defined by integrating the anisotropic part of tangential stress along the direction perpendicular to the interface [4]:

$$\gamma_\mathrm{LV} = \int_{-\infty}^{\infty} (p_\mathrm{N} - p_\mathrm{T}(z))\mathrm{d}z = \int_{-\infty}^{\infty} (p_0 - p_0 + p^t(z))\mathrm{d}z = \int_{-\infty}^{\infty} p^t(z)\mathrm{d}z\,. \tag{5}$$

Anisotropic part of tangential stress can be expressed in terms of difference of normal and tangential component of stress tensor: $p_\mathrm{N} - p_\mathrm{T}$. The surface tension can thus be interpreted as an anisotropic part of a force exerted between the portions of liquid on opposite sides of test surface of unit width that is perpendicular to the interface (see figure 4 (b)). From the construction of (5) we can see, that the definition of surface tension is independent of the vapour pressure. Although we did not go into detail about pressure tensor, we can mention that surface tension has a dependency on temperature. At higher temperatures the mean kinetic energy of liquid molecules is higher and consequently the repulsion is higher [1]. Furthermore, consistency of (5) with thermodynamic result (2) is revealed if we calculate an amount of work needed for a small reversible stretch of liquid-vapour system along the interface and simultaneous compression perpendicular to it to ensure constant volume.

The recently described distribution of forces can also be verified with numerical simulation of molecular dynamics [2] (see figure 5).

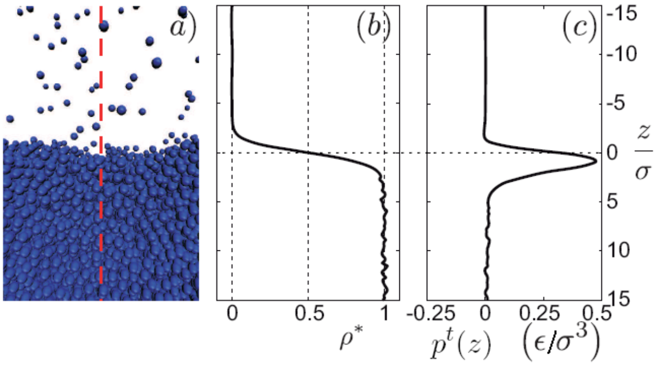


Figure 5: *Molecular dynamics simulation of liquid vapour interface using Lennard-Jones 6-12 potential* [2]. The vertical axis is in units of molecular scale σ. (a) Snapshot of a simulation. (b) Time-averaged normalized density profile $\rho^*(z) = (\rho(z) - \rho_{\mathrm{V}})/(\rho_{\mathrm{L}} - \rho_V)$ across the interface. ρ_{L} and ρ_{V} are bulk densities of liquid and vapour respectively. (c) Anisotropic part of tangential force per unit area exerted by the left part on the right part of the system.

The simulation corresponded to the one-component van der Waals liquid. The description of surface tension in this section is valid also for the case where one-component vapour is replaced by a mixture of gases. Description holds, whenever the nature of microscopic interaction result in short range repulsion and long range attraction on macroscopic scale. The value of surface tension and the profile of stress tensor of course depend on the concentration of components mixed into the liquid.

4 Wetting of the solid

Now we include also the solid. We will study some effects near contact line, which is a line where liquid vapour and solid phases are in contact.

The central quantity, that describes the composition of liquid, solid and vapour phase in the vicinity of contact line, is the equilibrium contact angle θ [3]. It is the angle between the liquid-vapour interface and the solid [3]. Precisely speaking, it is the angle between the two planes, one is tangential to the solid surface and the other that is best approximation for liquid-vapour interface from some $\sim 100 - 1000$ molecular distances from the contact line [3]. Curvature of the liquid-vapour interface in this regime can be neglected because for most experiments curvatures are macroscopic, thus on the millimeter scale [3]. Contact angle measures the extent to which solid is wet and can vary between 0 and π [6]. According to the value θ it is convenient to define four wetting regimes [6]:

- $\theta = 0$: completely wet solid
- $0 < \theta < \pi/2$: partially wet solid
- $\pi/2 < \theta < \pi$: partially dry solid
- $\theta = \pi$: completely dry solid .

In some literature [2, 3] they are only talking about regimes of partial and complete wetting, where the regime of partial wetting comprises all cases where $\theta > 0$.

In the regime of complete wetting the contact angle is only apparent, because the solid above is covered in a thin liquid film [2, 3]. The whole solid surface is actually wet. In the regime of partially wet and partially dry solid the contact line is well defined [3]. In the regime of partial wetting solid-liquid interactions are comparable by magnitude, so the liquid tends to wet the solid [2, 3]. However, in regime of partially dry solid interactions between solid and liquid molecules are much weaker than between liquid ones, therefore vapour is allowed to intrude between solid and liquid [6]. The case of completely dry solid is a limiting case of partially dry solid and a complete opposite to the complete wetting [6].

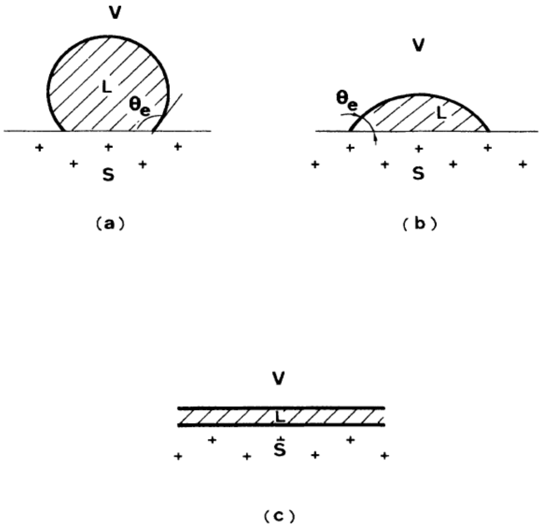


Figure 6: *Wetting regimes - a drop on a solid surface* [3]. In (a) and (b) we are in a regime the partially wet and partially dry solid respectively. Wetting is stronger in (b) than in (a). In (c) drop is completely flat, so we are in regime of complete wetting. An example for (a) is a drop of mercury on glass. Situation in example (b) is very common as we can think of water or oil on metallic surface. Water on glass behaves like in example (c).

We shall consider more thoroughly the case with partially wet solid. First, let us relate surface free energies $\gamma_{\mathrm{LV}}, \gamma_{\mathrm{SV}}, \gamma_{\mathrm{SL}}$ to the equilibrium contact angle. This was first done by Thomas Young in the beginning of the 19. century [3]. We can imagine, that we are attempting a small deformation of a horizontal liquid cylindrical cap near contact line. We denote an infinite cylinder, which has its long axis on contact line, as "core region", because it can have complex structure [3]. The system is in equilibrium, consequently there is no change in the free energy if we infinitesimally shift the contact line. Contact angle is fixed. The bulk energies of liquid and vapour do not change, neither does the energy of the core. Core is only shifted. The only subsystems of which energies are changed, are the interfaces between phases outside the core. In an example in figure (see figure 7) the solid-vapour interface is increased by $l\mathrm{d}x$, the solid-liquid interface is decreased by the same amount and liquid-vapour interface is decreased by $\cos(\theta) l\mathrm{d}x$ (see figure 7) [3]. Thus Young-Dupré relation reads: $\mathrm{d}F = (\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} - \gamma_{\mathrm{LV}}\cos(\theta))\, l\mathrm{d}x = 0$. Or more common:

$$\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}} = \gamma_{\mathrm{LV}}\cos(\theta)\,. \tag{6}$$

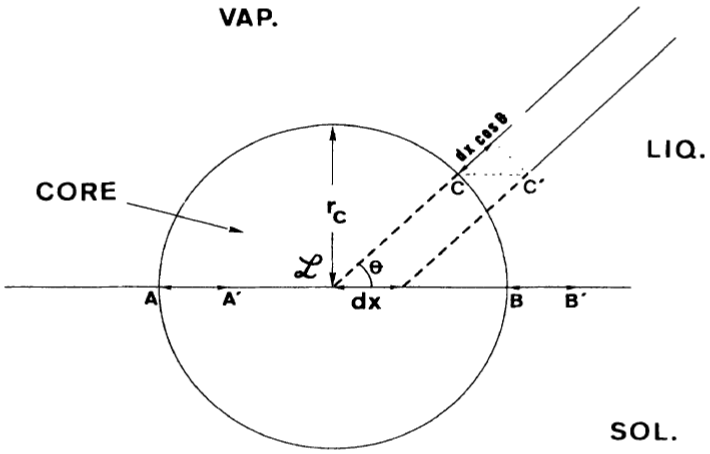


Figure 7: *Part of the liquid cylindrical cap, near contact line $\mathcal{L}$* [3]. The size of the core is usually $r_c \sim 10\sigma$ [3]. Curvature of liquid-vapour interface is negligible.

Young-Dupré's law is general. In the case of complete wetting it reads $\gamma_{\mathrm{SV}} = \gamma_{\mathrm{LV}} + \gamma_{\mathrm{SL}}$ [3]. Furthermore in the case $\theta > \pi/2$ the values $\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$ is negative and so is $\cos(\theta)$, the last can be seen if we imagined an obtuse contact angle in construction on figure 7. Because we used only thermodynamic arguments, the Young-Dupré's law should hold for all types of liquids regardless of their molecular composition and of the type of molecular interactions. Even though it has been around for two hundred years, it is still one of the central results of the theory of wetting [1].

4.1 Forces near liquid-solid interface

The Young-Dupré law is useful, because it gives us some insight into the shape of the liquid wedge that forms in the vicinity of the contact line. Yet it does not tell us anything about force distribution there, which is sometimes desired [2]. For example, in the past decades it became possible to measure small defects of soft solid matter which are the consequence of capillary forces near contact line [3]. First, we will consider forces near solid-liquid interface, then in the next subsection, we shall proceed to more complex case of forces in liquid wedge. Intermolecular interaction are again assumed to be comprised of long range attraction and short range repulsion.

Our first guess might be that there is a force per unit length dividing line at solid-liquid interface of magnitude γ_{LS} between the two parts of liquid, yet this is not true [2]. To begin with, the missing liquid, which is replaced by the solid, induces an anisotropy in liquid-liquid forces. The anisotropy leads to the surface tension γ_{LV} the same way as it does in the case of liquid-vapour interface [2]. Then we shall also include the effect of liquid-solid interactions. We are focusing on the capillary forces, thus gravity is ignored. Similarly as in liquid-vapour interface, we divide the liquid into two subsystems using control surface parallel to the interface (see figure 8(a)). Again we are considering forces on the dotted liquid system, which is the liquid not in contact with solid [2]. Solid exerts attractive forces in a direction only perpendicular to the interface. Forces have a reach of several molecular distances [2]. The attractive forces by the solid decrease with distance and are perfectly balanced by the repulsive forces from the rest of the liquid, which creates a "buffer zone" between considered liquid system and solid. As in previous case, we assume that the repulsive forces between liquid are isotropic, so there is also a force component tangential to the interface (see figure 8(b)) [2]. It was shown that the mentioned force parallel to the interface, which is the consequence of liquid-solid interactions, has a magnitude of $\gamma_{\mathrm{SV}} + \gamma_{LV} - \gamma_{\mathrm{SL}}$ per unit length [6].

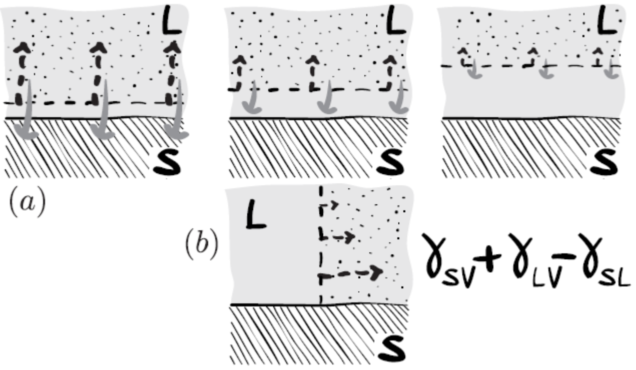


Figure 8: *Forces near solid liquid interface due to liquid-solid interactions* [2]. Forces considered are exerted on the subsystem of liquid, depicted as a dotted region. Solid subsystem is drawn as a white and dashed region. Attractive forces on considered subsystem are represented as gray arrows and repulsive ones as dashed black arrows. (a) Liquid subsystems are delimited with dashed line, parallel to the interface. Solid subsystem exerts attractive forces in a direction only perpendicular to the interface. (b) Liquid is now divided into two subsystems, delimited with a dashed line, perpendicular to the interface. The repulsion is isotropic, thus equal as in (a). Attraction due to liquid anisotropy is not taken into account.

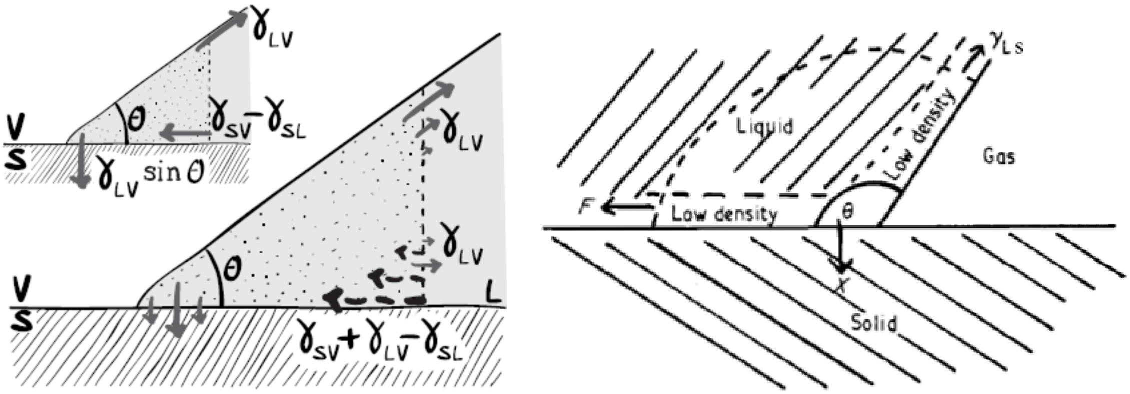
Combined with the liquid anisotropy effect, the force from the left to the right liquid subsystem is of magnitude $\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$ [2]. If $\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$ is positive, the force is repulsive and this leads to the regime of partial wetting ($0 < \theta < \pi/2$). Interactions between liquid and solid molecules lower the energy and thus wet solid surface is energetically favorable than a dry one. However, if $\gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$ is negative, it leads to the regime of partially dry solid.

4.2 Forces in the liquid corner

According to all previous analysis of forces, we will try to explain force distribution in the liquid wedge next to the contact line. As in the previous subsection we limit ourselves to the systems, where Lennard-Jones type intermolecular potential is dominant. The upper side of the wedge forms for example a small part of meniscus in a capillary tube.

The system is depicted on figure 9(a). It is an amount of liquid in a form of a wedge, separated from the rest of the liquid with an imaginary borderline. The wedge should be much bigger than several molecular distances, so a tipical length of 10-100 σ should be enough. The reason is that the effect of the third phase should be negligible at interfaces in the right corners (see figure 9(a)) [2, 3]. However it should not be too big, because are focusing on capillary effects, thus we are neglecting equilibrium pressure and gravity. Curvature of the wedge is neglected because it is usually on the scale of millimetres. The plane solid-liquid interface on the other hand, is a very rough approximation on such a scale [3].

Forces of molecular origin act on the wedge in its corners, which is near the interfaces (see figure 9(a)). In the right two corners forces correspond to the liquid on liquid forces near the liquid-vapour interface and similar forces near the liquid-solid interface. These forces have already been explained in previous sections. However, it is clear that these forces aren't enough to achieve mechanical balance. In the horizontal direction there indeed is a force balance and it reads $\gamma_{\mathrm{LV}} \cos(\theta) = \gamma_{\mathrm{SV}} - \gamma_{\mathrm{SL}}$, thus it is a mechanical equivalent to Young-Dupré's law [2]. In the vertical direction there is a component of surface tension force $\gamma_{\mathrm{LV}} \sin\theta$ that must be balanced. Therefore, a force component of magnitude $\gamma_{\mathrm{LV}} \sin\theta$ arises, which is localized in the vicinity of contact line and points downwards [2]. This also holds for obtuse contact angle (figure 9(b)) [4].



(a) (b)

Figure 9: *Forces on a liquid wedge* [2, 4]. (a) The system of interest-liquid wedge is depicted as dotted [2]. Characters S, L and V stand for solid, liquid and vapour respectively. (b) The contact angle is obtuse [4]. Liquid wedge is sorrounded by dashed line. Force χ is equal to $\gamma_{\text{LV}} \sin\theta$ and force $F = \gamma_{\text{SV}} - \gamma_{\text{SL}}$. We see that F points in the opposite direction than in (a), yet Young-Dupré's law holds.

The latter force has its origin in solid-liquid interaction near contact line [2]. Solid spans an infinite half-space, consequently the force on the above liquid has a direction purely normal to the solid-liquid interface [2]. Then we again consider the nature of forces. Solid on liquid repulsive forces again scale with the density of the liquid as they are considered purely as contact forces [2]. Far from the contact line repulsive and attractive forces exerted by solid on liquid perfectly balance each other [2]. The density of liquid should fall off continuously as we approach the vapour phase, yet the attractive forces diminish much more slowly [2]. That is because attractive forces have a longer range. Above description may seem a bit crude, but the solid-on-liquid force in the left corner has also been verified with some calculations [8].

In the end we can again remember that magnitude of mentioned capillary forces in the liquid wedge depend on the temperature and on the chemical structure of the materials. The change in temperature and chemical structure therefore usually changes the contact angle.

5 Conclusion

In this seminar we have introduced surface tension in a classical and in a more modern way. We have been trying to go beyond the description of surface tension as thin membrane under tension on liquid surface and find an interpretation in terms of molecular interactions. Thus we have found out that surface tension in wan der Waals liquids near liquid-vapour interface arises because of the anisotropy of attractive molecular forces near the interface. It spans some molecular distances from the interface and in this area the effect is much stronger than equilibrium or hydrostatic pressure.

We have also tried to put the surface tension in context of some more general capillary effects. First, we have presented some general concepts of capillarity such as the contact line, the equilibrium contact angle and different wetting regimes. We have also presented Young's law, which defines contact angle in terms of energies of interfaces. Again, from the nature of intermolecular interactions we have also analyzed microscopic force distribution in anisotropic system of liquid near the contact line of liquid, solid and vapour phase. This can give us better understanding of wetting phenomena, for example of drop forming.

References

[1] Rowlinson, J. S. and Widom, B. *Molecular theory of capillarity* (Dover publications, New York, 1982).

[2] Marchand, A., Weijs, J., Snoeijer, J. and Andreotti, B. *Why is surface tension a force parallel to the interface?*. Am. J. Phys. **79** (10) (2011).

[3] de Gennes, P. G. *Wetting: statics and dynamics*. Rev. Mod. Phys. **57**, 827-863 (1985).

[4] Berry, M. V. *The molecular mechanism of surface tension*. Physics Educations **6**, 79-84 (1971).

[5] Weijs, J. H., Marchand, A., Andreotti, B., Lohse, D. and Snoeijer J. H. *Origin of line tension for a Lennard-Jones nanodroplet*. Phys. Fluids **23**, 022001 (2010).

[6] Nijmeijer, M., Bruin, C., Bakker, A. and Van Leeuwen, J. *Wetting and drying of an inert wall by a fluid in a molecular-dynamics simulation*. Phys. Rev. A **42**, 6052-6059 (1990).

[7] Markovich, T., Andelman, D., Podgornik, R. *Surface tension of Electrolyte Solutions: A Self-consistent Theory*. Europhys. Lett. **106**, 16002 & 19903 (2013).

[8] Das, S., Marchand, A., Andreotti, B. and Snoeijer J. H. *Elastic deformation due to tangential capillary forces*. Phys. Fluids **23**, 072006 (2011).