Why is surface tension a force parallel to the interface?

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A paperclip can float on water. Drops of mercury do not spread on a surface. These capillary phenomena are macroscopic manifestations of molecular interactions and can be explained in terms of surface tension. We address several conceptual questions that are often encountered when teaching capillarity and provide a perspective that reconciles the macroscopic viewpoints from thermodynamics and fluid mechanics and the microscopic perspective from statistical physics. © *2011 American Association of Physics Teachers.*
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I. INTRODUCTION

Capillarity is one of the most interesting subjects to teach in condensed matter physics because its detailed understanding involves macroscopic thermodynamics,[1–3] fluid mechanics, and statistical physics.[4] The microscopic origin of surface tension lies in the intermolecular interactions and thermal effects,[5,6] while macroscopically it can be understood as a force acting along the interface or an energy per unit surface area. In this article, we discuss the link between these three aspects of capillarity using simple examples. We first discuss the standard problems faced by students and many researchers in understanding surface tension. We will see that the difficulty of understanding surface tension forces is often caused by an improper or incomplete definition of a system on which the forces act. We ask four basic questions, such as the one raised in the title, which we answer in the following. Contrary to many textbooks on the subject, we provide a picture that reconciles the microscopic, thermodynamic, and mechanical aspects of capillarity.

II. BASIC CONCEPTS AND PROBLEMS

A. The interface

Thermodynamic point of view. Following the pioneering work of Gibbs,[7] we introduce surface tension as the excess free energy due to the presence of an interface between two bulk phases. Consider a molecule in the vicinity of an interface, for example, a liquid-vapor interface. The environment of this molecule is different from the molecules in the bulk. This difference is usually represented schematically by drawing the attractive bonds between molecules, as shown in Fig. 1. We see from Fig. 1 that approximately half of the bonds are missing for a molecule at the interface, leading to an increase of the free energy. We thus define the surface tension from the free energy F per unit area:

$$\gamma_{LV} = \left(\frac{\partial F}{\partial A}\right)_{T,V,N},$$

(1)

for a system of volume V containing N molecules at temperature T. Hence, γ_{LV} is the energy needed to increase the interfacial area by one unit. Its dimension is $[\gamma_{LV}] = MT^{-2}$ (mass per time squared), and is usually expressed in N/m (force per unit length) or J/m^2 (energy per unit area).

The order of magnitude of the surface tension must be of the order of the bond energy ϵ divided by the cross section area σ^2 of a molecule, where σ is a fraction of a nanometer. The van der Waals interaction for oils leads to $\epsilon \sim k_B T \simeq (1/40)$ eV and thus $\gamma_{LV} \sim 0.02$ N/m. For water, hydrogen bonds lead to a higher value $\gamma_{LV} \sim 0.072$ N/m. For mercury, the high energy bonds ($\epsilon \sim 1$ eV) lead to an even higher surface tension $\gamma_{LV} \sim 0.5$ N/m.

Mechanical point of view. In fluid mechanics, the surface tension is not defined in terms of a surface energy but rather as a force per unit length. In the bulk of a fluid at rest, two sub-parts of a fluid exert a repulsive force on one another, which is called the pressure. If the surface separating these two subsystems crosses the liquid-vapor interface, an additional force needs to be taken into account: surface tension. As shown in Fig. 2, the surface tension is a force tangent to the surface and normal to the contour separating the two subsystems. The total force is proportional to the width W of the contour. Contrary to pressure, surface tension is an attractive force.
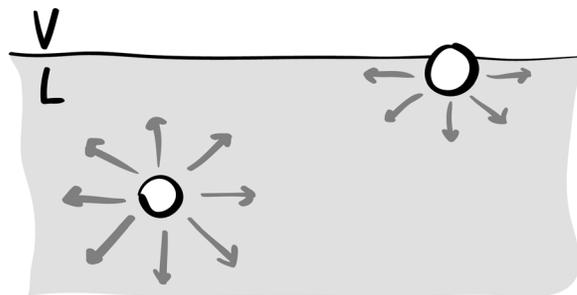

Fig. 1. Sketch showing the missing intermolecular bonds close to the liquid-vapor interface, giving rise to an increase in the free energy per unit area, that is, the surface tension.
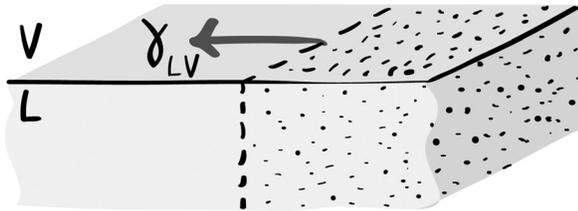
Fig. 2. Sketch showing the surface tension as a force per unit length exerted by one subsystem on the other. The system on which the forces act is the dotted region. The force is parallel to the interface and perpendicular to the dividing line.

The link between mechanics and thermodynamics is provided by the virtual work principle. If we move a contour of width W by a length $d\ell$, the area of the interface of the subsystem considered increases by $Wd\ell$. Consequently, the free energy is increased by $\gamma_{LV}Wd\ell$. The free energy equals the work done by the surface tension force, which means that this force is parallel to the interface, normal to the contour, and has a magnitude $\gamma_{LV}W$. Per unit length, the surface tension force is thus γ_{LV}.

For students, the link between mechanics and statistical physics is much less obvious than the link between mechanics and thermodynamics. We clearly see in Fig. 1 that the molecule at the interface is subject to a net force (which would be represented by the sum of the vectors) along the direction perpendicular to the interface. However, we just argued from the mechanical point of view, that the force is parallel to the interface. This difference in perspective leads to the first key question of this article:

Question 1: Why is surface tension a force parallel to the interface even though it seems obvious that it must be perpendicular to it?

B. The contact line

Thermodynamic point of view. A standard method for determining the liquid-vapor surface tension is to measure the force required to pull a metallic plate (usually made of platinum) out of a liquid bath. This force is related to the liquid-vapor surface tension γ_{LV}, as is usually explained by a diagram similar to Fig. 3(a). Imagine that the plate is moved vertically by a distance $d\ell$. The area of the liquid-vapor interface is not changed by this motion, and thus the corresponding interfacial energy is unaffected. However, the motion leads to a decrease of the immersed solid-liquid interface area by $Wd\ell$, while the solid-vapor interface increases by the same amount. In other words, part of the wetted surface is exchanged for a dry surface, which leads to a change of the free energy $dF = (\gamma_{SV} - \gamma_{SL})Wd\ell$, where γ_{SV} and γ_{SL} are the solid-vapor and solid-liquid surface tensions, respectively. This energy is provided by the work done due to the force required to displace the plate by $d\ell$. Hence, this force must be equal to $(\gamma_{SV} - \gamma_{SL})W$.

To relate this force to the value of the liquid-vapor surface tension γ_{LV}, we invoke Young's law for the contact angle θ see Fig. 3(b) and the following discussion). When the three interfaces between the solid, liquid, and vapor join at the contact line, the liquid makes contact with the substrate at an angle θ given by[8]

$$\gamma_{LV}\cos\theta = \gamma_{SV} - \gamma_{SL}. \qquad (2)$$

By using Eq. (2), the force exerted on the plate can be expressed as $W\gamma_{LV}\cos\theta$, and thus, we have designed a tensiometer.

Mechanical point of view. From the mechanical point of view, we can interpret the force required to maintain the plate out of the bath as the surface tension acting parallel to the liquid-vapor interface [see Fig. 3(a)]. By symmetry, the total force exerted on the solid is vertical (the horizontal components sum to zero). By projecting the surface tension force onto the vertical direction and by multiplying the length W of the contact line, we obtain $W\gamma_{LV}\cos\theta$.

By a similar argument, we usually interpret Young's law for the contact angle as the balance of forces at the contact line [see Fig. 3(b)]. By a projection along the direction parallel to the solid substrate, we obtain $\gamma_{SL} + \gamma_{LV}\cos\theta = \gamma_{SV}$, which is the same as Eq. (2). This force interpretation is a common source of confusion for students:

Question 2: From Fig. 2(b), there seems to be an unbalanced force component in the vertical direction $\gamma_{LV}\sin\theta$. What force is missing to achieve equilibrium?

Question 3: Why do we draw a single force acting on the contact line for the plate [Fig. 3(a)], while for Young's law we need to balance all three forces [see Fig. 3(b)]?

Actually, when measuring a surface tension using the plate technique, we often use a platinum plate to be sure that the liquid completely wets the solid. In that case $\gamma_{SV} - \gamma_{SL} > \gamma_{LV}$ and Young's law does not apply. In this case, the thermodynamic and mechanical approaches give conflicting answers:

Question 4: For complete wetting, is the force on the plate given by γ_{LV} or by $\gamma_{SV} - \gamma_{SL}$?

C. Brief answers

We start with a short overview of the answers to the questions we have raised. We emphasize that the thermodynamic result (that is, from the virtual work principle) always gives the correct total force. If we want to know the local force distribution, which cannot be extracted from thermodynamics, it is imperative that the system on which the forces act is properly defined. Confusion regarding the forces is often caused by an improper or incomplete definition of such a system.

Answer 1: The schematic of Fig. 1 represents only the attractive intermolecular forces. The real force balance
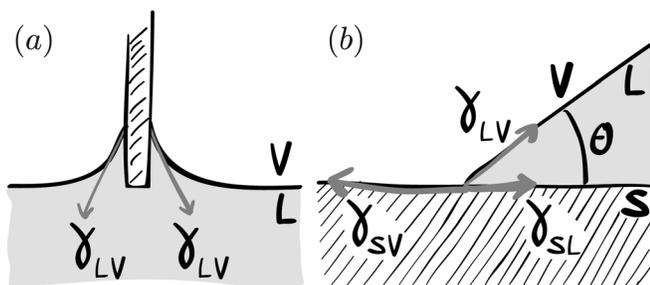

FIG. 3. (a) Experimental method for determining the liquid-vapor surface tension. The force per unit length needed to pull a plate from a bath of liquid is equal to $\gamma_{LV}\cos\theta$, where θ is the equilibrium contact angle. (b) A traditional way to interpret Young's law as a force balance of surface tensions. Question 2: Why is there no force balance in the normal direction? Question 3: Why do we draw a single surface tension force in (a) (γ_{LV}) while there are three in (b) (γ_{LV}, γ_{SV}, and γ_{SL})?

requires both repulsive and attractive interactions between liquid molecules.

To answer questions related to the contact line, it is crucial to specify the system of molecules on which the forces are acting:

Answer 2: In Young's law, the system on which the forces act is a corner of liquid bounded by the contact line. γ_{LV} is the force exerted on this system inside the liquid-vapor interface, but the forces exerted by the solid on the corner are incomplete in Fig. 3(b). An extra vertical force on the liquid, caused by the attraction of the solid, exactly balances the upward force $\gamma \sin \theta$

Answer 3: To obtain the force on the plate, the system to consider is the solid plate. In this case, the force exerted by the liquid on the solid is equal to $\gamma_{\text{LV}} \cos \theta$ per unit length.

Answer 4: The correct vertical force on the plate is $W\gamma_{\text{LV}} \cos \theta$. For complete wetting ($\theta = 0$), the virtual work principle can be applied, but only when taking into account the prewetting film.

III. MICROSCOPIC INTERPRETATION OF CAPILLARITY

A. The liquid state

To address the origin of capillarity, we have to understand how a liquid phase and a vapor phase can coexist. To do so, we consider the van der Waals equation of state, which can account for the liquid-gas phase transition:[5,9]

$$P = \frac{kT}{v-b} - \frac{a}{v^2}, \tag{3}$$

where P is the pressure and v is the volume per molecule. Equation (3) corrects the ideal gas law to incorporate the effect of intermolecular forces. The constant b introduces repulsion between molecules as an excluded volume effect: the pressure diverges when the total volume per molecule reaches a minimal size b. In this limit, the molecules are densely packed and constitute a liquid phase. In this phase, the volume per molecule no longer depends on pressure, which means that the liquid phase is incompressible. Ultimately, this effect comes from the repulsion of the electron clouds of the molecules, due to the Pauli exclusion principle. The constant a represents the long-range attraction between molecules which finds its origin in the dipole-dipole interaction (van der Waals attraction).

Equation (3) explains how a low density gas phase can coexist with a high density liquid phase. This coexistence requires the pressures to be identical on both sides of the interface, despite the striking difference in density. In a gas, where $v = v_g$ is large, most of the energy is kinetic ($a/v_g^2 \ll P$), and the pressure is $P \simeq kT/v_g$. In the liquid phase, the volume per unit molecule is almost in the incompressible limit and $v = v_l \approx b$. This strong repulsive effect ($kT/(v_l - b) \gg P$) is counterbalanced by the presence of attractions ($a/v_l^2 \gg P$) so that, for the same temperature, the pressure in the liquid phase can be in equilibrium with the pressure in the gas phase, giving rise to a stable liquid-vapor interface.

How can a liquid at the same time be repulsive and attractive? A single pair of atoms can only attract or repel each other, depending on the distance separating them. Their interaction is shown schematically in Fig. 4. The steep poten-
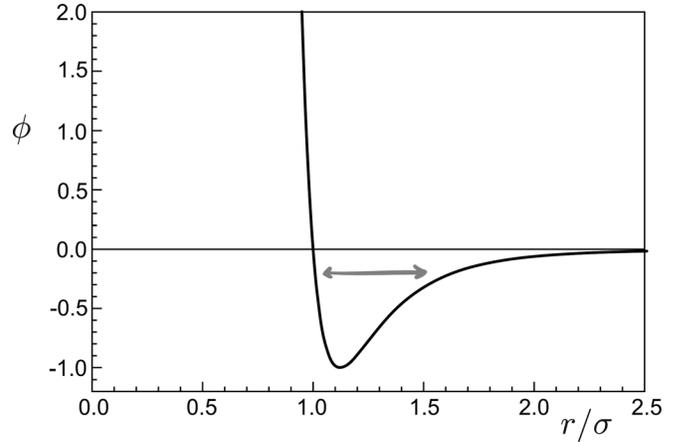

Fig. 4. Lennard-Jones intermolecular potential ϕ. The interaction is strongly repulsive for intermolecular distances $r < \sigma$. At large distances, the molecules are attracted to one another. The gray arrow points to the presence of thermal fluctuations, which, in a liquid, lead to substantial variations of the intermolecular distance.

tial reflects the short-range repulsion, and the negative tail represents the long-range attraction. The balance of attractive and repulsive interactions in Eq. (3) only has a statistical meaning: some particles attract each other while others repel. The existence of both repulsion and attraction is what makes liquids very different from solids like polycrystals. In such solids, thermal effects are often negligible and molecules in the same region are either all compressed (if the region is submitted to an external compression) or all attracted to each other (if the region is submitted to an external tension).

The difference between a solid and a liquid can be traced to the importance of thermal fluctuations, that is, the kinetic energy of the molecules. In the solid phase, these fluctuations are small with respect to the potential energy, that is, $k_B T \ll \epsilon$, where ϵ is the energy scale for the intermolecular forces. As a consequence, the system explores only a small region of the potential. Hence, the solid is either in the compressed or in the tensile state. In contrast, the liquid phase is characterized by large fluctuations, for which $k_B T \sim \epsilon$. A broad range of the potential is therefore sampled by molecules in the same region of space (see Fig. 4). The case $k_B T \gg \epsilon$ corresponds to a gas phase of weakly interacting particles that is dominated by kinetic energy.

B. The liquid-vapor interface: Question 1

We now consider the liquid-vapor interface in more detail. Figure 5(a) shows a snapshot of the interface obtained in a molecular dynamics simulation of molecules interacting with the Lennard-Jones potential.[10–12] The corresponding time-averaged density profile is plotted in Fig. 5(b). The transition from the high density liquid to the low density gas takes place in a very narrow region that is a few molecules wide. To determine the capillary forces we need to divide the system along the direction normal to the interface into two subsystems [see Fig. 5(a)]. We consider the force exerted by the left subsystem on the right subsystem through a small vertical surface at the separation of the subsystems and at the vertical position z. This force is proportional to the area of this small surface so that we can define the force per unit area, which is the stress, exerted by the left on the right as a function of z. This stress can be decomposed into two
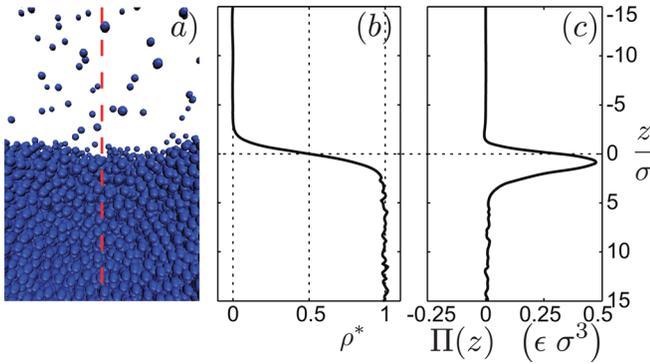
Fig. 5. The liquid-vapor interface. The vertical axis is in units of σ. (a) Snapshot of a molecular dynamics simulation of a liquid-vapor interface using the Lennard-Jones potential. (b) Time-averaged normalized density profile $\rho^*(z)$ across the interface. (c) Tangential force per unit area exerted by the left part on the right part of the system. The plot shows the difference $\Pi = p_{NN} - p_{TT}$ between the normal and tangential components of the stress tensor.

contributions: the pressure P, which is the same in the vapor and the liquid bulk, plus an extra stress $\Pi(z)$ acting along the direction parallel to the interface [see Fig. 5(c)]. The profile of this stress anisotropy shows that there is a force localized at the interface, acting in the direction parallel to the interface. This force is spread over a few molecular diameters, which is the typical thickness of the density jump across the interface. The integrated contribution of this force is equal to γ_{LV} per unit length, the surface tension. The simulations show that surface tension really is a mechanical force.

Now that we have found that there is a parallel force localized at the interface, we turn to Question 1. Why is the tension force parallel and not normal to the interface? We first note that Fig. 1 depicts only the attraction between molecules. A more complete picture also incorporates the repulsive contributions to the internal pressure, as denoted by the dashed arrows in Fig. 6. Away from the surface there is perfect force balance due to the symmetry around a molecule. Near the interface, however, the up-down symmetry is broken. To restore the force balance in the vertical direction, the upward repulsive arrow (dashed) has to balance the downward attractive arrow (solid). In the direction parallel to the interface, the symmetry is still intact, thus automatically ensuring a force balance parallel to the interface. This balance means that along the direction parallel to the interface, there is no reason why the attractive forces should have the same magnitude as the repulsive forces. In practice, the attractive forces are stronger, which gives rise to a positive surface tension force.
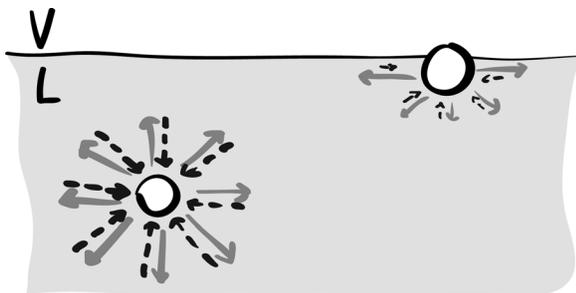

Fig. 6. Sketch showing repulsive (dashed black arrows) and attractive (gray arrows) forces in the bulk and at the surface.

C. Separate roles of attraction and repulsion

We still need to explain why the intermolecular forces give rise to such a strong tension along the surface. This question was addressed by Berry,[6] who noted the separate roles of attraction and repulsion. The key observation is that, to a good approximation, the repulsive contribution to the pressure is isotropic while attraction is strongly anisotropic. The reason is that the repulsion is short ranged due to the hard core of the molecules and can be thought of as a "contact force." As such, repulsion is not very sensitive to the changes in the structure of the liquid around the molecules, and in particular near the interface where repulsion remains equally strong in all directions.[12] In contrast, the long-range nature of the attractive forces make them very sensitive to the structure of the liquid. The difference between the ranges of the attractive and repulsive interactions is the origin of the observed pressure anisotropy near the interface that generates the surface tension force.

To see how the anisotropy works out in detail it is useful to divide the liquid into two subsystems using an imaginary surface parallel to the liquid-vapor interface, as shown in Fig. 7(a). The force exerted on the dotted subsystem by the rest of the liquid results from the superposition of attractive (vertical gray arrows) and repulsive (dashed black arrows) interactions [see Fig. 7(a)]. Because the subsystem is in equilibrium, these attractive and repulsive components must balance each other. The magnitude of the attractive force increases with the size of the attracting region because the density increases as the system moves from the vapor toward the liquid phase. The magnitude of the attraction saturates to the bulk value when the imaginary surface is a few molecular sizes from the interface. We then divide the liquid into two subsystems using an imaginary surface perpendicular to the liquid vapor interface [see Fig. 7(b)]. We can now see that the repulsive short-range forces are isotropic, which means that the repulsion (dashed black arrows) exerted by the left side on the subsystem (dotted region) increases with
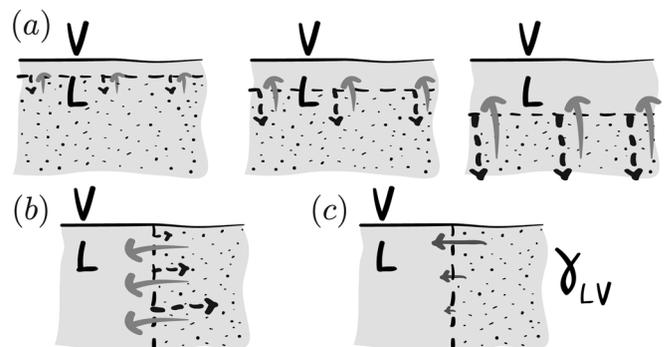

Fig. 7. Forces exerted on a subsystem of liquid (dotted region) by the rest of the liquid (gray region without dots). (a) The subsystem is the lower part of the liquid and is separated from the interfacial zone by a line parallel to the liquid-vapor interface. The subsystem (dotted region) is subjected to an attractive force (gray arrows) and a repulsive force (dashed black arrows) exerted by the rest of the liquid (gray region without dots). The forces must balance each other. (b) The liquid is divided along a line perpendicular to the interface. The subsystem considered (the dotted region on the right) is subjected to an attractive force (gray arrows) and to a repulsive force (dashed arrows) exerted by the rest of the liquid (gray region without dots). Because the repulsive force is isotropic, it has the same magnitude as in (a) and therefore decays close to the surface. In contrast, the attractive force is nearly constant and remains almost unchanged close to the surface. (c) This construction leads to a net attractive force from one side on the other.

depth in a way analogous to that in Fig. 7(a). In contrast, the strength of the attraction has a much weaker dependence on depth; for simplicity, we draw it with a constant magnitude which equals the attraction in the bulk. As a result, there is a net attraction of the subsystem by the rest of the liquid [see the dark gray arrow in Fig. 7(c)].

D. The liquid-solid interface

Forces near the liquid-solid interface. We now consider the liquid-solid interface (see Fig. 8). In this case, two effects superimpose. Due to the presence of the solid, there is a lack of liquid in the lower half-space (hatched region in Fig. 8). The missing liquid induces an anisotropy of the attractive liquid-liquid force in the same way as it does for the liquid-vapor interface. Hence, as in Fig. 7(c), the left-hand side of the liquid exerts a net attractive force γ_{LV} per unit length on the right-hand side subsystem. The other effect is due to the liquid-solid interaction. In the same way as for the liquid-vapor interface, we divide the liquid into two subsystems using an imaginary surface parallel to the interface, as shown in Fig. 8(a). The attraction by the solid (gray arrow) decreases with distance and is perfectly balanced by the short range liquid-liquid repulsive force (dashed arrows). We then divide the liquid into two subsystems using an imaginary surface perpendicular to the liquid solid interface [see Fig. 8(b)]. If we assume that the liquid-liquid repulsion is isotropic, the left part of the liquid exerts a net repulsive force on the right subsystem (dotted region). This force is induced by the influence of the solid and, surprisingly, it is not equal to γ_{SL}. Instead, it has been shown[11] that this force is equal to $\gamma_{SV} + \gamma_{LV} - \gamma_{SL}$, as will be motivated in more detail in the following.

To combine these two effects, we subtract the unbalanced attractive force due to the absent liquid (γ_{LV}) from the repulsive force due to the solid ($\gamma_{SV} + \gamma_{LV} - \gamma_{SL}$) to find the net repulsive force between the subsystems: $\gamma_{SV} - \gamma_{SL}$.

Solid-liquid interaction and the surface tensions. Let us motivate why the strength of the solid-liquid interaction does
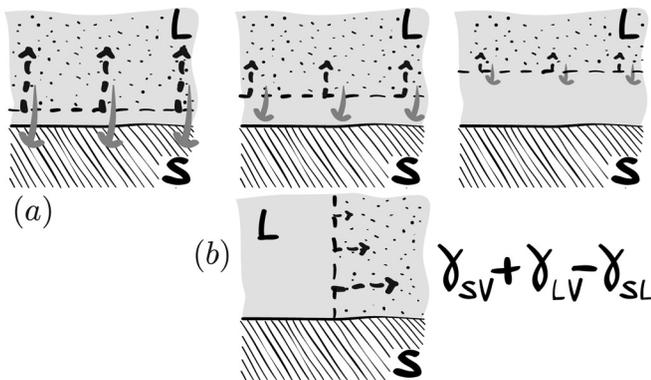

Fig. 8. Forces exerted by the solid (dashed line) on a subsystem of liquid (dotted region). The attractive liquid-liquid interactions treated in Fig. 7 are not considered. (a) The liquid subsystem is semi-infinite. It is delimited by a line parallel to the liquid-solid interface, at different distances above it. The subsystem is subjected to an attractive force (gray arrows) exerted by the solid and to a repulsive force (dashed arrows) exerted by the rest of the liquid (gray region without dots). Because the subsystem is in equilibrium, these forces must balance each other. (b) The liquid is divided along a line perpendicular to the interface. Only the horizontal force components are shown. The solid exerts no horizontal attraction. Because the repulsive interactions are isotropic, this construction results in an horizontal repulsive force $\gamma_{SV} + \gamma_{LV} - \gamma_{SL}$ exerted by one side on the other.
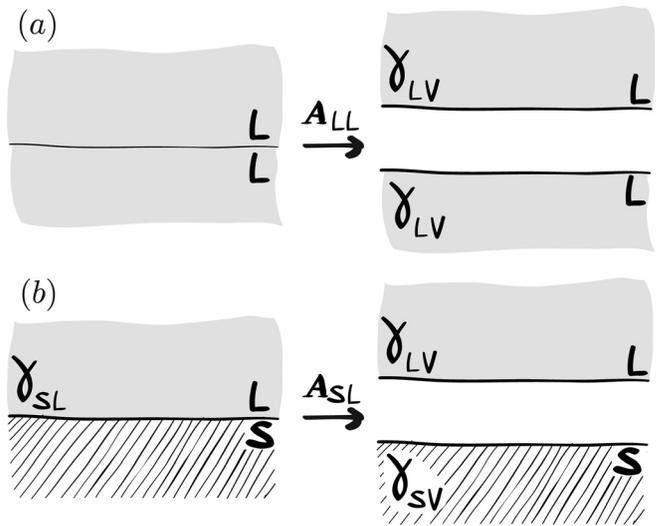
Fig. 9. Relation between adhesion work and surface tensions. (a) To split a liquid volume into two semi-infinite volumes, we have to create two liquid-vacuum interfaces, which costs energy $A_{LL} = 2\gamma_{LV}$. (b) To create a solid-liquid interface, we first need to create a liquid-vacuum and solid-vacuum interface, which costs energy $\gamma_{SV} + \gamma_{LV}$. Joining the liquid-vacuum and solid-vacuum interfaces yields an energy reduction $A_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$ due to the solid-liquid attraction.

not couple directly to the solid-liquid surface tension γ_{SL}, but to the combination $\gamma_{SV} + \gamma_{LV} - \gamma_{SL}$.[1,13] This feature is also crucial for understanding the wetting phenomena discussed in Sec. IV.

The solid-liquid surface tension represents the free energy needed to create a solid-liquid interface. To make such an interface, we first have to "break" the bulk solid and the bulk liquid into two separate parts, and then join these solid and liquid parts together. The breaking of the liquid is depicted schematically in Fig. 9(a) (it works similarly for the solid). The corresponding energy is the "work of adhesion" A_{LL} due to liquid-liquid attractions (A_{SS} for the solid). This breaking gives rise to a surface tension $2\gamma_{LV} = A_{LL}$ ($2\gamma_{SV} = A_{SS}$), because the liquid (solid) is connected to a vacuum at this intermediate stage. When joining the solid-vacuum and liquid-vacuum interfaces, the attractive solid-liquid interaction reduces the surface energy by the solid-liquid work of adhesion A_{SL} [see Fig. 9(b)]. Hence, the resulting solid-liquid surface tension becomes

$$\gamma_{SL} = \gamma_{SV} + \gamma_{LV} - A_{SL}. \tag{4}$$

From Eq. (4), we find that the strength of the solid-liquid adhesion is

$$A_{SL} = \gamma_{SV} + \gamma_{LV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta) \tag{5}$$

In the last step, we used Young's law for the equilibrium contact angle. As a consequence, the magnitude of the capillary forces induced by solid-liquid attractions is $A_{SL} = \gamma_{LV}(1 + \cos\theta)$ and not γ_{SL}.

IV. MICROSCOPIC INTERPRETATION OF WETTING

The question of the force balance is even more complicated in the vicinity of the contact line, where the liquid-vapor interface meets the solid. It is important to note that

the contact line does not represent any material. Instead it is an imaginary line that marks the separation between wetted and dry parts of the solid. The question "What is the force on the contact line?" is thus ill-posed, because there are no molecules on which such a force would act. Only a collection of matter can be submitted to a force. Therefore, care should be taken to properly define the systems that play a role near the contact line, which are the liquid near the contact line and the solid underneath it. In the following, we will show how a careful consideration of all the forces on the appropriate material systems leads to proper force balances, consistent with the thermodynamic predictions.

All results and sketches provided in this section, some of which may appear counterintuitive, are consistent with a density functional theory for microscopic interactions[14,15] and molecular dynamics simulations.[12]

A. Force on a liquid corner: Question 2

Consider the forces on the wedge-shaped liquid corner in the vicinity of the contact line, as shown in Fig. 10. We will now explain Young's force construction from Fig. 3(b) and answer Question 2: What happens to the force balance normal to the solid-liquid interface?

There are two types of forces acting on the liquid molecules inside the subsystem: interactions with the solid and interactions with other liquid molecules outside the subsystem. We first consider the solid-on-liquid forces. We see that because the solid spans an infinite half space, every liquid molecule experiences a resultant force which is normal to the solid-liquid interface: the left-right symmetry of the solid ensures that there is no force component parallel to the interface. Far from the contact line at the solid-liquid interface, this attractive force is balanced by a repulsive force, as shown in Fig. 8. Because the repulsive force is continuous

and zero outside the droplet, the repulsive force must decay close to the contact line. This decay means that there is an unbalanced attractive force which is strongly localized in the vicinity of the contact line. It has been shown[16] that this force per unit length is equal to $\gamma_{LV} \sin \theta$.

The existence of this force has recently been challenged.[17,18] To show that this force must exist to achieve equilibrium, we consider the droplet shown in Fig. 11. If we choose the droplet as the system and recognize that the force in the interior of the droplet at the liquid-solid interface (small arrows) is due to the Laplace pressure $2\gamma_{LV}\kappa$ (with κ the curvature $1/R$), we see that the attractive force at the contact line must be $\gamma_{LV} \sin \theta$ to achieve a force balance.[19–23] This picture provides the answer to Question 2: the downward solid-on-liquid force is not drawn in Fig. 3(b). This missing force has often been interpreted as a reaction from the solid,[2] whose existence is demonstrated experimentally by the elastic deformation of soft solids below the contact line.[22–25] Here, we clarify the molecular origin of this normal force.[16]

To finalize the force construction near the contact line, we return to the wedge shown in Fig. 10(b). Because the solid can exert only a normal force on the liquid, all parallel force components drawn in Young's construction are purely due to the liquid molecules outside the corner. The force drawn along the liquid-vapor interface can be understood directly from the tension γ_{LV} inside the liquid-vapor interface (see the discussion of Fig. 7). A similar force arises at the solid-liquid interface (see Fig. 8), which is repulsive and has the magnitude $\gamma_{SV} - \gamma_{SL}$. Including these forces gives a perfect force balance on the liquid corner, as seen in Fig. 10(a). It can be easily verified that even the resultant torque is zero for this force construction. As such, it provides a more physical alternative to the classical picture of Young's law.

B. Liquid-on-Solid force: Question 3

The measurement of surface tension shown in Fig. 3(a) relies on the force exerted by the liquid on the solid plate. Again, we emphasize the importance of a proper definition of the system on which the forces act. In this case, the system is the solid on which the liquid rests. The situation is thus very different from the forces on the liquid corner, which are in equilibrium so that the resultant force is zero. This difference provides the key to Question 3. In Fig. 3(a), the total force exerted by the liquid on the solid is represented by the
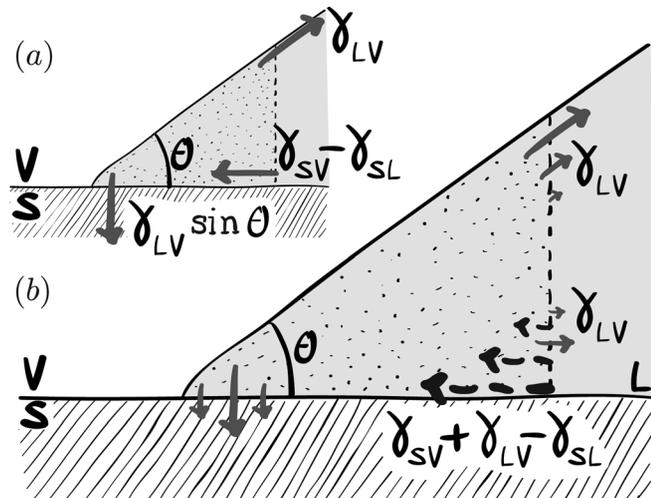

Fig. 10. Solid and liquid forces acting on a liquid subsystem (dotted region) near the contact line. (a) Sketch of a wedge of liquid near the contact line with the three forces exerted on the system. (b) Each of the three corners of this system must be treated differently. The upper right corner is at the liquid vapor interface. Following Fig. 7, the rest of the liquid exerts a net attractive force parallel to the interface equal to γ_{LV} per unit length. The lower right corner is at the liquid solid interface. Following Figs. 7 and 8, the rest of the liquid exerts a repulsive force $\gamma_{SV} - \gamma_{SL}$. The liquid near the solid-liquid interface is attracted by the solid. This force is balanced everywhere by repulsion at the solid-liquid interface, except in the vicinity of the contact line.
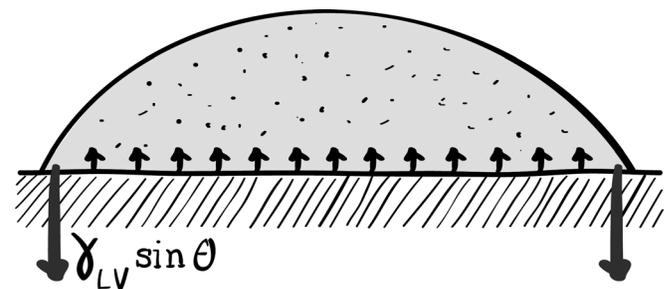

Fig. 11. Forces acting on a liquid drop (dotted area). The system is in equilibrium so the sum of all external forces must be zero. Due to Laplace pressure, there is a repulsive force exerted by the solid on the liquid across the liquid-solid interface (upward black arrows). In the vicinity of the contact line, repulsion and attraction of the liquid by the solid do not balance each other. Therefore, the solid attracts the liquid with a vertical force equal to $\gamma_{LV} \sin \theta$ per unit length (downward dark gray arrows).

resultant $\vec{\gamma}_{LV}$, and Fig. 3(b) represents the balance of the forces acting on the liquid wedge.

Forces near the contact line. We turn again to the microscopic description of the forces in the vicinity of the contact line. It turns out that the normal component of the force exerted on the solid is equal to $\gamma_{LV} \sin\theta$, consistent with the macroscopic picture of a tension force pulling along the liquid-vapor interface. The parallel component of the liquid-on-solid force does not have the expected magnitude $\gamma_{LV} \cos\theta$, but $\gamma_{LV} + \gamma_{SV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta)$. This unexpected magnitude can be understood as follows. Figure 12(a) illustrates that the tangential force component originates from the long-range attraction between solid and liquid molecules. We previously demonstrated that the strength of this solid-liquid adhesion is $A_{SL} = \gamma_{LV}(1 + \cos\theta)$. Hence, there is no reason why the total force on the solid should be $\gamma_{LV} \cos\theta$. A density functional theory calculation confirms a tangential liquid-on-solid force of magnitude $A_{SL} = \gamma_{LV}(1 + \cos\theta)$.[16]

The physics of this surprising result is illustrated by Fig. 12. The macroscopic intuition that the resultant surface tension force pulls along the liquid-vapor interface would predict a force to the left whenever the contact angle $\theta > 90°$. However, it is clear from the sketch of the attractive forces that the sum of all the parallel components must be oriented toward the liquid (right side in the figure). This orientation stems from the asymmetry between the amount of liquid attracting the solid molecules on both sides of the contact line: there are always more liquid molecules on the right side of the contact line in Fig. 12. This behavior is consistent with the parallel force $\gamma_{LV}(1 + \cos\theta)$, but not with a force $\gamma_{LV} \cos\theta$ (which changes sign at $\theta = 90°$). Note that when considering the force exerted by the solid on the liquid, this asymmetry does not occur because the solid is left-right symmetric, and therefore there is no tangential component. This difference between the forces acting on the solid or on the liquid again illustrates that a detailed force interpretation crucially relies on the definition of the system.

Global force balance: curvature of solid-liquid interface. To solve the apparent discrepancy between the tangential force $\gamma_{LV}(1 + \cos\theta)$ and the thermodynamic result we discussed in Sec. II B, which was consistent with a tangential force $\gamma_{LV} \cos\theta$, we have to consider all the forces exerted by the liquid on the solid, not just the forces near the contact line. The key point is that the submerged solid bodies cannot be flat everywhere and the liquid-solid interface must be curved. If the interface separating the solid from the liquid is flat, the net normal force is locally zero because repulsion balances attraction (far away from the contact line). When the interface is curved, the repulsive force inside the liquid is enhanced due to the curvature, in a way similar to the Laplace pressure. As shown in Fig. 13, the presence of a curved half-space of liquid acts on the solid and creates an unbalanced liquid-on-solid force $\gamma_{LV}\kappa$ per unit area. Density functional theory calculations[16] show that the resultant pressure couples only to γ_{LV} and not to γ_{SL}. As we will show, this supplementary force is exactly what is needed to restore consistency between the microscopic and thermodynamic forces.

An excellent demonstration of this effect is the long debated case of a "floating-pin" under zero gravity, as shown in Fig 14. Although a floating pin in a system with gravity leaves a visible depression in the liquid-vapor interface near the contact line [see Fig. 14(e)], the zero-gravity condition ensures that the interface has constant curvature, that is, it is straight everywhere. Because the liquid-vapor interface is flat, the vertical position of the pin depends on the equilibrium contact-angle alone and not on the density ratio of the materials involved. As shown in Fig. 12, the liquid-on-solid forces near the contact lines are not oriented along the liquid-vapor interface, but point toward the interior of the
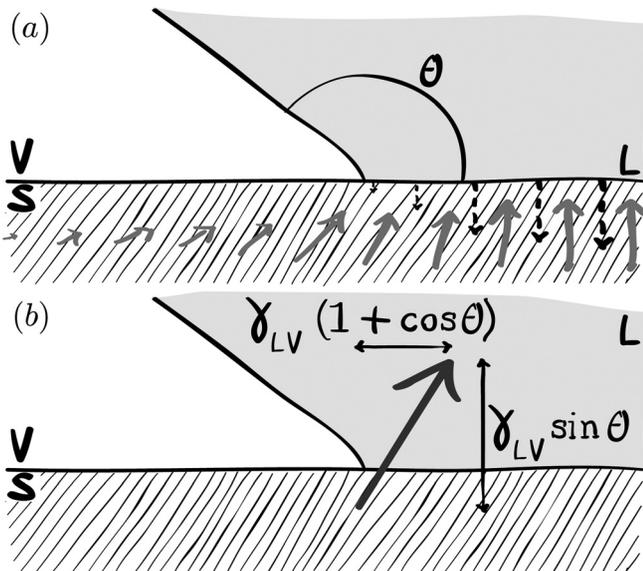

Fig. 12. Forces acting on the solid subsystem (hatched areas) by the liquid (gray areas) near the contact line. (a) Distribution of forces acting on the solid near the contact line. Due to the attraction of the liquid, the solid is attracted toward the liquid (solid gray arrows). The absence of liquid on the left part of the contact line ensures the tangential force is toward the liquid, even for $\theta > 90°$. The repulsion (dotted arrows) arises from the contact force at the solid-liquid interface. Far from the contact line, repulsion and attraction balance each other. (b) The resultant force acting on the solid near the contact line. The net normal force is $\gamma_{LV} \sin\theta$, and the parallel force $\gamma_{LV} + \gamma_{SV} - \gamma_{SL} = \gamma_{LV}(1 + \cos\theta)$.
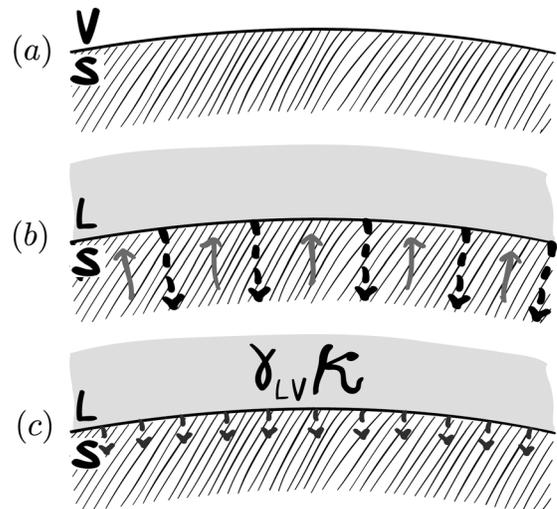

Fig. 13. Forces acting on a solid at the solid-liquid interface. (a) Without liquid, there is neither repulsion nor attraction. (b) When liquid is present there is repulsion and attraction. However, the repulsion is not completely balanced at this curved interface, because there is more liquid in this geometry than in a plane geometry. (c) The resulting force is analogous to the force created by the Laplace pressure at liquid-vapor interfaces. This force is $\gamma_{LV}\kappa$ per unit surface, where $\kappa > 0$ is the curvature of the liquid. This expression only shows a dependence on the liquid-liquid interactions because the curvature has an effect only through the missing liquid matter.
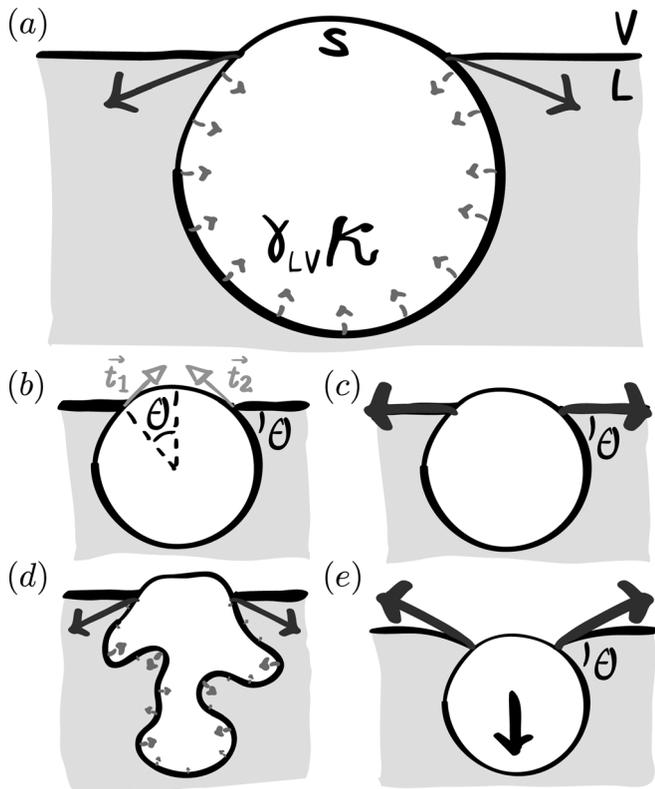
Fig. 14. (a) Schematic of a pin floating at the surface of a liquid under partial wetting conditions and in zero gravity. The downward thin gray arrows are the forces exerted by the liquid on the pin located in the vicinity of the contact line. The small light gray arrows show the Laplace pressure $\gamma_{LV}\kappa$ acting on the solid due to the curvature κ of the solid-liquid interface. (b) The quantity θ denotes the contact angle, and $\vec{t}_1$ and $\vec{t}_2$ are unit vectors tangential to the pin, pointing upward, at the two contact lines. (c) The thick gray arrows show the resultants of the capillary forces in (a), which apply on each half of the pin. They reduce to forces tangential to the liquid-vapor interface at the contact lines. This schematic does not show the distribution of capillary forces. (d) Distribution of the capillary forces for an irregular shape. Because the integral over the curvature is equal to the sum of the two tangential vectors at the contact lines, the resultant is independent of the shape of the body. It is thus the same as in (c). (e) Pin floating at the surface of a liquid under gravity. The upward thick gray arrows are the resultants of capillary forces. They balance the effect of gravity (corrected by the Archimedes force), shown as the downward black arrow.

liquid. The total force resulting from the contributions of the two contact lines is vertical and downward. Additionally, the curvature of the solid-liquid interface creates a normal force distributed over the entire immersed surface of the solid of magnitude $\gamma_{LV}\kappa$ per unit surface [see Fig. 14(a)]. Integrating over the curvature of the submerged surface from one contact line to the other gives the resultant of the Laplace pressure:

$$\gamma_{LV} \int_1^2 \kappa \vec{n} \, dS = \gamma_{LV}(\vec{t}_2 + \vec{t}_1) \tag{6}$$

where $\vec{t}_1$ and $\vec{t}_2$ are unit vectors tangential to the pin, pointing upward. Therefore, the resultant is orientated upward and is equal to $2\gamma_{LV}\sin\theta$ per unit depth [see Fig. 14(b)]. It balances exactly the downward forces induced close to the contact lines [see Fig. 12(b)], and hence the pin is in equilibrium. This result is independent of the shape of the body [see Fig. 14(d)].
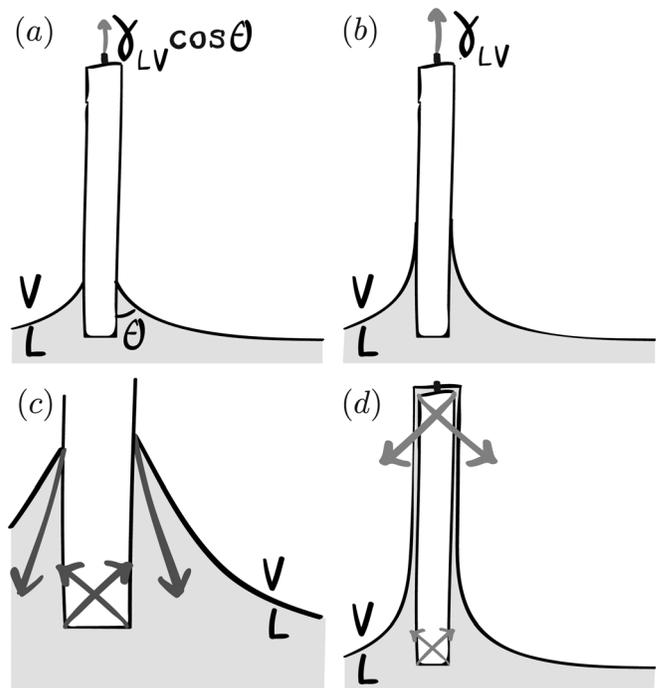

Fig. 15. Force per unit length of the contact line needed to keep a plate in equilibrium in a bath in (a) partial and (b) complete wetting. (c) Partial wetting. The vertical force at the contact line, equal to $\gamma_{LV}(1 + \cos\theta)$, is balanced by the Laplace pressure induced by the curvature of the plate. Note that any plate shape would lead to the same resultant force because the integral of the curvature over the surface reduces to the local tangents at the contact line [see Fig. 14(d)]. (d) Complete wetting case. Due to the mesoscopic pre-wetting film, whose thickness is exaggerated in the figure, there is no contact line; thus, there is no force located near the apparent macroscopic contact line. The forces are related only to the Laplace pressure. The curvature of the solid gives a zero resultant force, because the solid is completely immersed in the liquid. Besides the curvature of the liquid acts on the solid only in the pre-wetting zone because the Laplace pressure is compensated by gravity in the meniscus. The resultant force per unit length is equal to γ_{LV}.

The same principle applies to the partially wetted plate of Fig. 3(a): the force exerted by the fluid on the plate results from two contributions as shown schematically in Fig. 15(c). There is the vertical force component (per unit length) due to the vicinity of the contact line: $\gamma(1 + \cos\theta)$ (see Fig. 12). There also are submerged surfaces of the plate where a localized curvature exists at the corners. This curvature induces a Laplace force on the pin [see Fig. 14(d)], which results in a net upward force γ_{LV} per unit length of contact line and means that the total force (per unit length of contact line) on the plate is $\gamma_{LV}\cos\theta$, in agreement with the thermodynamic result.

Complete wetting: Question 4. For complete wetting, Young's law for the contact angle is no longer applicable. Instead, the apparent contact angle θ vanishes because the three surface tensions do not balance each other:

$$\gamma_{SV} - \gamma_{SL} > \gamma_{LV}. \tag{7}$$

Physically, there is no real contact line in this configuration [see Fig. 15(b)], but there is a meniscus where the liquid-vapor interface approaches the solid. Beyond the meniscus, there exists a mesoscopic liquid film called a prewetting film, which covers the solid completely [see Fig. 15(d)]. The existence of an apparent contact line is due only to the effect

of gravity: on a flat surface, the liquid would simply spread. The interface between the liquid and vapor phases consequently has two regions. In the lower region, the meniscus can be described by the balance between the Laplace pressure and the hydrostatic pressure

$$\gamma_{LV}\kappa = \rho g z, \tag{8}$$

where z is the height above the bath (thus, no additional constant is needed) and κ is the curvature of the interface. If we introduce the capillary length $\ell_\gamma = \sqrt{\gamma_{LV}/\rho g}$, Eq. (8) can be written as $\ell_\gamma^2 \kappa = z$. In the upper region, there is the prewetting film whose thickness $h(z)$ is determined by the balance between the gravitational potential and the disjoining pressure $\Pi(h)$ defined as the potential energy per unit volume at the surface of a liquid layer of thickness h. It describes the attraction of the solid in the layer of liquid. Therefore, the balance is[1,13]

$$\Pi(h) = \rho g z. \tag{9}$$

Because the prewetting film is flat, the contribution of the Laplace pressure can be neglected ($\kappa = 0$) in this regime. The pressure scales as

$$\Pi(h) \simeq \frac{(\gamma_{SV} - \gamma_{SL} - \gamma_{LV})\sigma^2}{h^3}, \tag{10}$$

for films where $h \gg \sigma$, σ is a length on the order of the molecular size. The pressure vanishes in the limiting case $\gamma_{SV} = \gamma_{SL} + \gamma_{LV}$, which can be interpreted as the situation for which the interaction is the same with the liquid and with the solid. Then, we do not expect any influence of the thickness h on the energy.

We equate gravity and the disjoining pressure, Eq. (9), and obtain the thickness profile in the prewetting region:

$$h(z) \simeq \left[\frac{(\gamma_{SV} - \gamma_{SL} - \gamma_{LV})\sigma^2}{\rho g z}\right]^{1/3}. \tag{11}$$

In the vicinity of the apparent contact line, where the two zones must match, the thickness is thus of order $l_\gamma^{1/3}\sigma^{2/3}$. Because l_γ is the order of millimeters and σ is the order of nanometers. From the microscopic point of view, the solid is completely surrounded by a semi-infinite layer of liquid ($h \gg \sigma$). Therefore, the only forces acting on a solid in complete wetting are normal contact forces, such as Laplace pressures. There are no contact line forces such as those described in Fig. 12(b).

The forces exerted by the liquid on the solid are related to the curvature of the liquid-solid interface and inside the prewetting film to the curvature of the liquid-vapor interface [see Fig 15(d)]. If integrated over the whole submerged solid, the curvature of the solid gives a zero resultant force, whereas the curvature of the liquid is integrated only where the prewetting film exists. As a result, the resultant force is vertical and has an amplitude γ_{LV} per unit length of the apparent contact line.

This result is consistent with the thermodynamic perspective. Because the solid is covered by a liquid layer much thicker than the molecular size, the surface tension above the apparent contact line is not γ_{SV} but is $\gamma_{SL} + \gamma_{LV}$, because the plate is always completely submerged. In essence, this coverage means that the plate never leaves the liquid bath when

the plate is pulled upward. When moving, there is no change of the solid-vapor interface area (it remains zero) or of the solid-liquid interface area (which is the total area of the plate). The only change occurs at the liquid-vapor interface area, which is increased, and the required pulling strength is thus γ_{LV} per unit length of the apparent contact line.

V. SUMMARY

We have raised simple questions about capillarity that many students face. By studying the interfaces from a microscopic perspective, we have provided answers to these questions, and reconciled thermodynamics and statistical physics.

We have provided a mechanical perspective about why there exists an attractive force parallel to interfaces, which is called the surface tension. The absence of liquid above the liquid-vapor interface creates an attractive anisotropic force within a few molecular lengths from the interface, whereas the repulsion remains isotropic and scales with the local density of the fluid. The attractive anisotropy leads to a strong localized force parallel to the interface called the surface tension. This anisotropy and corresponding tangential force occurs at liquid-solid interfaces as well, where there is also a half-space of liquid missing.

The problems that occur when constructing force pictures at interfaces often arise from an improper definition of the system on which the forces act. By considering a corner of liquid near the contact line as a system, we proposed an alternative to Young's construction [see Fig. 3(b)]. The analysis lets us locate and understand the different forces, in particular, the attractive force exerted by the solid. This new force construction leads to perfect mechanical equilibrium, where the net force and the torque balance.

When looking at the force that is exerted by the liquid on the solid near the contact line we find that this force is not $\gamma_{LV}\cos\theta$, but is $\gamma_{LV}(1 + \cos\theta)$. Moreover, a normal stress is exerted in all the regions of any curved solid-liquid interface, so that the liquid pulls the solid when the latter is convex. This force is equivalent to the usual Laplace pressure. We have to take both these forces into account to obtain the net force from thermodynamics. The advantage of this microscopic force description is that it provides a simple answer to a problem that has been controversial: the floating pin paradox.[17,18,26]

The drawings and several relations in this article are based on results obtained using density functional theory in the sharp-kink approximation.[16] This model can be used to make quantitative predictions of the force distributions in the liquid and in the solid.

We realize that a detailed picture of the microscopic forces is not necessarily the most accessible for teaching purposes. In particular, when introducing the basic concepts of capillarity, it is much simpler to work from the thermodynamic perspective: energy minimization naturally yields the equilibrium conditions, and the resultant forces can be calculated from the virtual work principle. Nevertheless, our analysis provides a number of insights that are useful when teaching capillarity:

1. To determine the capillary forces it is crucial to explicitly specify the system (a specific collection of matter) to which the forces are applied.
2. The surface tensions γ_{SL} and γ_{SV} do not pull on the solid.
3. The global force exerted on the solid by the liquid can be calculated by adding the contributions of the Laplace

pressure inside the liquid and a localized surface tension force γ_{LV} parallel to the liquid-vapor interface. Although this force construction gives the correct answer, it does not reflect the true microscopic distribution of liquid-on-solid forces.

4. In contrast, the resultant force on the liquid near the contact line does involve the surface tensions γ_{LV}, γ_{SL}, and γ_{SV}.

5. The classical construction of Fig. 3(b) to explain Young's law does not accurately represent the force balance. A complete picture is provided in Fig. 10(a).

We hope that the force construction of Fig. 10(a) will be used to explain Young's law in Eq. (2). It is conceptually simple, clarifies the system to which forces are applied, and represents perfect mechanical equilibrium. That is, besides a balance of normal and tangential components, the forces also exert a zero torque.

We note that the virtual work principle yields the correct resultant force on a solid, but cannot recover the true microscopic force distribution. A knowledge of such a force distribution is crucial when we want to take into account how a solid is elastically deformed by the contact line.[19–21] Even though these deformations can be as small as a few nanometers, they can be measured using modern experimental techniques.[22–25] This experimental access renews the fundamental interest in the microscopic details of capillarity.[16]

ACKNOWLEDGMENTS

[1] P.-G. de Gennes, "Wetting" Statics and dynamics," Rev. Mod. Phys. **57**, 827–863 (1985).

[2] P.-G. de Gennes, F. Brochard-Wyart, and D. Quéré, *Capillarity and Wetting Phenomena* (Springer, New York, 2004).

[3] D. Bonn, J. Eggers, J. Indekeu, J. Meunier, and E. Rolley, "Wetting and spreading," Rev. Mod. Phys. **81**, 739–805 (2009).

[4] J. Kirkwood and F. Buff, "The statistical mechanical theory of surface tension," J. Chem. Phys. **17**, 338–343 (1949).

[5] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Dover Publications. Mineola, NY, 1982).

[6] M. Berry, "The molecular mechanism of surface tension," Phys. Educ. **6**, 79–84 (1971).

[7] J. W. Gibbs, *The Collected Works of J. Willard Gibbs* (Yale U. P., London, 1957).

[8] T. Young, "An essay on the cohesion of fluids," Philos. Trans. **95**, 65–87 (1805).

[9] J.-P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, 3rd ed. (Academic, San Diego, 2006).

[10] J. Indekeu, "Line tension near the wetting transition – Results from an interface displacement model," Physica A **183**, 439–461 (1992).

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

[12] J. H. Weijs, A. Marchand, B. Andreotti, D. Lohse, and J. H. Snoeijer, "Origin of line tension for a Lennard-Jones nanodroplet," Phys. Fluids **23**, 022001-1–11 (2011).

[13] J. N. Israelachvili, *Intermolecular and Surface Forces* (Academic, San Diego, 1991).

[14] C. Bauer and S. Dietrich, "Quantitative study of laterally inhomogeneous wetting films," Eur. Phys. J. B **10**, 767–779 (1999).

[15] T. Getta and S. Dietrich, "Line tension between fluid phases and a substrate," Phys. Rev. E **57**, 655–671 (1998).

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

[17] R. Finn, "The contact angle in capillarity," Phys. Fluids **18**, 047102-1–7 (2006).

[18] R. Finn, "Comments related to my paper "The contact angle in capillarity," Phys. Fluids **20**, 107104-1–4 (2008).

[19] A. Rusanov, "Theory of wetting of elastically deformed bodies. 1. Deformation with a finite contact angle," Coll J. USSR **37**, 614–622 (1975).

[20] A. Carre, J. Gastel, and M. Shanahan, "Viscoelastic effects in the spreading of liquids," Nature **379**, 432–434 (1996).

[21] L. R. White, "The contact angle on an elastic substrate. 1. The role of disjoining pressure in the surface mechanics," J. Colloid Inter. Sci. **258**, 82–96 (2003).

[22] R. Pericet-Camara, G. K. Auernhammer, K. Koynov, S. Lorenzoni, R. Raiteri, and E. Bonaccurso, "Solid-supported thin elastomer films deformed by microdrops," Soft Matter **5**, 3611–3617 (2009).

[23] R. Pericet-Ca?mara, A. Best, H.-J. Butt, and E. Bonaccurso, "Effect of capillary pressure and surface tension on the deformation of elastic surfaces by sessile liquid microdrops: An experimental investigation," Langmuir **24**, 10565–10568 (2008).

[24] Y. Wang, B. Bhushan, and X. Zhao, "Nanoindents produced by nanobubbles on ultrathin polystyrene films in water," Nanotechnology **20** 045301-1–6 (2009).

[25] Y.-S. Yu and Y.-P. Zhao, "Elastic deformation of soft membrane with finite thickness induced by a sessile liquid droplet," J. Colloid Inter. Sci. **339**, 489–494 (2009).

[26] I. Lunati, "Young's law and the effects of interfacial energy on the pressure at the solid-fluid interface," Phys. Fluids **19**, 118105-1–4 (2007).