

The physical description of elementary surface phenomena: Thermodynamics versus mechanics

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A unified treatment of elementary surface phenomena based on the formalism of thermodynamics is presented and compared to more familiar treatments based on the formalism of Newtonian mechanics. Emphasis is put on the surface free energy concept rather than on surface tension, not only because the former is more fundamental, but also because the latter may mislead if pushed too far. The examples discussed (Young–Laplace and Young–Dupré equations, and capillary rise) can be easily described with the help of the Helmholtz function, and clearly show some of the advantages of the thermodynamic approach. In particular, several misleading results appearing in elementary treatments can be avoided by using this approach. It is concluded that: (i) thermodynamics and physical chemistry courses should favor the formalism of thermodynamics rather than mechanics when dealing with surface phenomena; and (ii) when the mechanical approach is still preferred, some weak points in the standard derivations (e.g., the existence of an adhesion force in the explanation of the Young–Dupré equation and the nature and balance of forces in capillary rise) should be properly dealt with. © 1995 American Association of Physics Teachers.

INTRODUCTION

Surface phenomena are important not only to physics but also to neighboring disciplines such as physical chemistry, life and health sciences, and chemical engineering. The study of these phenomena has found an established place in elementary treatments of these disciplines, but not in our current introductory and intermediate physics courses. Most recent textbooks either present only a brief account of surface phenomena^{1–3} or ignore them completely.⁴ This brief account often appears before the chapters devoted to thermodynamics, and thus these phenomena are described by using mechanical rather than thermodynamic arguments. Though this procedure may certainly be suitable if one wishes to save time and put emphasis on classical physics, it should however be recognized that surface phenomena are far from being old-fashioned. Indeed, they continue to play a prominent role in research fields at the interface of physics with chemistry, biology, and engineering.^{5,6} The vigorous, multidisciplinary interest in surface phenomena has also resulted in many different (and sometimes confusing) treatments reflecting the particular training and interest of their authors. Surprisingly even some thermodynamics texts have used mechanical rather than thermodynamic arguments when dealing with surface phenomena.⁷

We propose here a unified treatment of *elementary* surface phenomena that relies on the formalism of thermodynamics^{8–12} rather than on that of mechanics. With the help of very simple models, some of the advantages of the thermodynamic approach are shown:

(1) Surface phenomena are explained in terms of *surface free energy* instead of *surface tension*. This procedure is not only closer to the currently accepted viewpoint^{5,13,14} but also is free from misleading results that occasionally arise when surface tension is used.

(2) Students have the opportunity to see that the classical methods of thermodynamics also apply to physical systems other than gases, solutions, etc. In addition, they see the application of the Helmholtz function, which is seldom employed in the classroom examples of thermodynamics courses, but is very suited to this study.

(3) Thermodynamics gives a broad view of the subject and

suggests new ways of understanding the physical concept of surface tension and deriving familiar results like the Young–Laplace and the Young–Dupré equations, and capillary rise.

It should however be recognized that since the formalism of thermodynamics requires an understanding of the Helmholtz function, most of the material presented here may not be appropriate for an introductory physics course. Nevertheless, we believe that this description will be useful in intermediate physics courses (thermodynamics, surface science, physical chemistry) for scientists and engineers.

PHYSICAL CONCEPT OF SURFACE TENSION

In this section we consider a pure condensed phase (solid or liquid) in equilibrium with its vapor (i.e., one-component, two-phase systems). The description of these heterogeneous systems must include the physical properties of matter in the bulk phases as well as the effect of the phase boundary or *interphase*. The interphase is defined as the thin region across which the physical properties vary smoothly from those of the bulk condensed phase to those of the bulk vapor. However, the actual limits of the interphase are ill-defined, which gives rise to different approaches to its study.⁸ Fortunately, the intermolecular forces extend only over a short range (of the order of 10 Å for simple molecules)¹⁵ and then the interphase can be considered as infinitely thin. Consequently, we will follow the so-called Gibbs description of the interphase, and regard the system as two homogeneous bulk phases separated by a geometrical surface of zero volume, known as the *interface*.

It is observed experimentally that the reversible increase of the area of the interface by a small amount dA , keeping the temperature and the volume of the two phases constant, requires some external work δW_{ext} proportional to dA :

$$\delta W_{\text{ext}} = \gamma dA, \quad (1)$$

where the proportionality coefficient γ is positive and is given the name of *surface tension* from the comparison of Eq. (1) with the expression of the work necessary to extend the area of an elastic membrane under tension τ by dA :

$$\delta W_{\text{ext}} = \tau dA. \quad (2)$$

The need for this external work can be easily explained in terms of a molecular description. The cohesion of condensed phases is due to intermolecular forces. The interaction of a given molecule with its (nearest) neighbors leads to a reduction of its potential energy, i.e., intermolecular forces act to stabilize the system. However, the molecules at the surface region of this condensed phase have a smaller number of nearest neighbors, and therefore their potential energy is not decreased by as much as in the interior of the condensed phase. In other words, if the zero of potential energy is considered that of the molecules in the interior of the condensed phase, the molecules at the surface region have a positive potential energy.^{14,16} In the vapor phase, intermolecular forces are negligible because of the large distance between nearest neighbors so the molecules in the vapor phase will have a positive potential energy with respect to the condensed phase (i.e., the latent heat of vaporization or sublimation). Since the number of nearest neighbors in the surface region is nearly half the number in the condensed phase, the potential energy per molecule in the surface region can be estimated as half the energy per molecule in the vapor phase.¹⁴

The increase in area requires a proportional increase in the number of molecules at the interface. Since these molecules move from the bulk of the condensed phase to the interface, there is a net increase in potential energy associated with this motion. The theorem of conservation of mechanical energy equates the external work with the increase in potential energy. The surface tension γ represents the rate of increase in (potential) energy of the interface with respect to the interfacial area.¹⁷

Another interpretation of the coefficient γ can be obtained from fundamentals of thermodynamics. We already know that the system can be regarded as two homogeneous bulk phases, denoted α and β in the following paragraphs, which are separated by the interface. When attempting to describe surface phenomena by the methods of thermodynamics, the question of which thermodynamic function should be used naturally arises. Since the independent variables characterizing this system are the temperature, which is considered constant in this treatment, the volumes of the phases α and β , V^α and V^β , respectively, and the area of the interface A , the most adequate thermodynamic function for the study of this system is the Helmholtz free energy F .¹⁸ Now, we consider that the bulk phases as well as the interface contribute to F and write

$$F = F_\alpha + F_\beta + F_\sigma, \quad (3)$$

where the subscript σ denotes magnitudes related to the interface. This decomposition of F into three separate contributions is possible because of the short range of intermolecular forces. Molecular behavior is independent of position when the molecules remain far from the interface, so in the two bulk phases the major contribution to the free energy is proportional to the phase size (number of moles, mass, or volume). However, the molecular behavior close to the interface is different and even though the interface is considered as a mathematical surface without volume,¹⁹ it accounts for the difference in the properties of matter in the interphase with respect to the bulk phases, and therefore it contributes to the free energy of the system.^{16,20}

The change in the Helmholtz free energy is equal to the work of reversible isothermal expansion of phases α and β and the interface, which gives us

$$\begin{aligned} dF &= dF_\alpha + dF_\beta + dF_\sigma \\ &= -\delta W_\alpha - \delta W_\beta - \delta W_\sigma = -p_\alpha dV_\alpha - p_\beta dV_\beta + \gamma dA. \end{aligned} \quad (4)$$

[Note that δW_σ is the work carried out by the interface so its sign is opposite to that of the external work against the interface given in Eq. (1).] Equation (4) now permits the interpretation of γ as the change in the free energy of the interface F_σ per unit area at constant temperature

$$\gamma = \left(\frac{\partial F_\sigma}{\partial A} \right)_T. \quad (5)$$

This interpretation of γ is considered to be the most fundamental.^{5,9,10,13,14}

Finally note that the surface free energy γ is determined by the intensive state of the bulk phases, which in turn is completely determined by T , p_α , and p_β . The fact that γ is independent of the surface area A makes this system quite different from solid elastic films. In solid elastic films the number of molecules is constant while the area changes, so that both the average distance between neighboring molecules and the forces between them change. In contrast, the change in area of the interface takes place via an increase in the number of molecules, and the average intermolecular distance and force remain practically constant. Therefore, the surface free energy γ does not depend on the surface area.

APPLICATIONS

In this section we study the mechanical equilibrium of different systems composed of two or more homogeneous phases and their interfaces. In thermodynamic terms, the condition of equilibrium requires the minimization of the Helmholtz function, while in mechanical terms the vector resultant of the forces (i.e., surface tensions) acting on the system must vanish. There is, apparently, a third alternative which consists in using the principle of virtual work. However, since dF at constant temperature equals the reversible work δW , this principle is practically equivalent to the minimization of the Helmholtz function.

Young-Laplace equation

We are interested here in determining the condition of mechanical equilibrium of an isothermal, closed system made up of a spherical liquid drop of radius r (phase α) immersed in its vapor (phase β). The two phases are considered to be at chemical equilibrium, so that their masses do not change. Since the system is closed, the total volume remains constant and any change in V_α is accompanied by an opposite change in V_β :

$$dV_\alpha = -dV_\beta. \quad (6)$$

In order to lower the energy of the system, the area of the interface must be reduced. This, however, causes a decrease in the volume of the liquid phase V_α , which in turn increases the energy of the system. The size of the liquid drop is determined by a compromise between these two tendencies, so that the overall reversible work done by the system is zero under equilibrium conditions, and dF in Eq. (4) vanishes.¹⁹ The condition of mechanical equilibrium is then expressed as

$$p_\alpha - p_\beta = \gamma \frac{dA}{dV_\alpha} \quad (7)$$

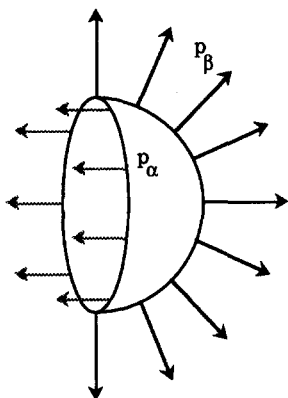


Fig. 1. Imaginary section of a spherical liquid drop in two hemispheres. The arrows pointing radially outwards represent forces due to the pressure difference ($p_\alpha - p_\beta$). The arrows pointing to the left represent forces due to surface tension.

which, for the case of the spherical drop under consideration, leads to the well-known Young–Laplace equation

$$p_\alpha - p_\beta = \frac{2\gamma}{r}. \quad (8)$$

Alternatively, the Young–Laplace equation is often derived from mechanical arguments.^{7,11,21} On the one hand, the surface tension acts to reduce the volume of the drop and increase the inner pressure p_α . On the other hand, the pressure difference between phases α and β acts to increase the volume of the drop. The equilibrium condition is then achieved when these two tendencies counterbalance each other. If only a hemisphere is considered (Fig. 1), the force due to surface tension is equal to $2\pi r\gamma$, where $2\pi r$ is the length of the circumference C of the hemisphere H . The force due to pressure difference is $p_\alpha - p_\beta$ times the projected area of the hemisphere, i.e., $(p_\alpha - p_\beta)\pi r^2$. Therefore, the equilibrium condition leads to Eq. (8).

Young–Dupré equation

In this second case study we are interested in the condition of mechanical equilibrium for three homogeneous phases in contact. The homogeneous phases are bounded by three interfaces which join in a line of triple contact, and the equilibrium condition of the system is expressed as the equilibrium of the line of triple contact. In particular we consider here a “sessile drop,” i.e., a liquid drop in equilibrium on a (plane) solid surface (Fig. 2). In this case the equilibrium will be achieved when the solid S and the liquid L are also in equilibrium with the surrounding vapor V .

If we assume that the three homogeneous phases are in chemical equilibrium, then the change in the Helmholtz function associated with a change in the drop shape is

$$dF = \gamma_{LV}dA_{LV} + \gamma_{LS}dA_{LS} + \gamma_{SV}dA_{SV}, \quad (9)$$

where A_{LV} , A_{LS} , A_{SV} , γ_{LV} , γ_{LS} , and γ_{SV} are the areas and surface free energies (surface tensions in mechanical terms) of the liquid–vapor, liquid–solid, and solid–vapor interfaces, respectively. All these surface free energies are positive because the molecular interactions in the bulk condensed phases are more effective in reducing the (potential) energy

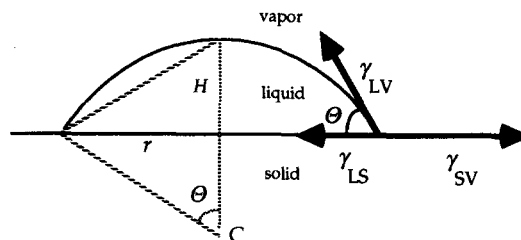


Fig. 2. Sessile drop on a flat solid surface. The liquid–vapor interface is a spherical cap whose center of curvature is at C . Neumann’s construction for the equilibrium of the line of contact is also depicted.

of the system than the molecular interactions at the interfaces. We might think there must be a tendency to reduce A_{LV} , A_{LS} and A_{SV} , because of the positive signs of these surface free energies; however, the changes in the solid phase can usually be neglected, and the total surface area of the solid phase is considered to be constant:

$$dA_{LS} = -dA_{SV}. \quad (10)$$

(In fact, solid–solid and solid–vapor molecular interaction play a negligible role in surface phenomena at normal temperatures.¹³)

Thus, we arrive at the following expression for the change in the Helmholtz function:

$$dF = \gamma_{LV}dA_{LV} + (\gamma_{LS} - \gamma_{SV})dA_{LS}. \quad (11)$$

We already know that γ_{LV} acts to reduce A_{LV} . The coefficient $(\gamma_{LS} - \gamma_{SV})$ can be either positive or negative, as this term contains essentially the influence of liquid–liquid intermolecular forces, which act to reduce A_{LS} , and liquid–solid intermolecular forces, which act to increase A_{LS} . If the liquid–solid interactions are negligible, the energy associated with the liquid–solid interface is practically the same as the sum of the energies associated with the separate liquid–vapor and solid–vapor interfaces and $\gamma_{LS} \approx \gamma_{SV} + \gamma_{LV}$. The sessile drop then behaves as when it is fully immersed in its vapor and adopts the shape of a sphere. If $\gamma_{LS} = \gamma_{SV}$, then the molecules in the liquid part of the interphase behave just like molecules in bulk liquid phase (i.e., liquid–solid interactions are like liquid–liquid interactions) and the drop adopts the shape of a hemisphere. Finally, if $\gamma_{LS} < \gamma_{SV} - \gamma_{LV}$ the liquid–solid intermolecular forces are so effective in reducing the energy of the system that no equilibrium can be achieved and the drop spreads out on the solid surface (i.e., $A_{LS} = A_{LV} \rightarrow \infty$).

For the sake of simplicity we consider a sessile drop with the shape of a spherical cap of height H and base of radius r (see Fig. 2). In order to derive the equilibrium condition of the sessile drop, we consider its volume V fixed, and write

$$dF = \gamma_{LV}dA_{LV} + (\gamma_{LS} - \gamma_{SV})dA_{LS} = 0, \quad (12)$$

where^{22–24}

$$V = \frac{1}{6}\pi H(3r^2 + H^2), \quad (13)$$

$$A_{LV} = \pi(r^2 + H^2), \quad (14)$$

$$A_{LS} = \pi r^2 \quad (15)$$

and

$$dV = \pi H r dr + \frac{1}{2}\pi(r^2 + H^2)dH = 0, \quad (16)$$

$$dA_{LV} = \frac{r^2 - H^2}{r^2 + H^2} 2\pi r dr \quad (V \text{ fixed}), \quad (17)$$

$$dA_{LS} = 2\pi r dr \quad (V \text{ fixed}). \quad (18)$$

If the angle of contact between the liquid–vapor and liquid–solid interfaces is denoted by Θ (see Fig. 2), then Eq. (12) can be written as

$$dF = [\gamma_{LV} \cos \Theta + \gamma_{LS} - \gamma_{SV}] 2\pi r dr = 0 \quad (19)$$

since the application of the cosine theorem to the dotted triangle in Fig. 2 gives $\cos \Theta = (r^2 - H^2)/(r^2 + H^2)$. The equilibrium condition then takes the final form

$$\cos \Theta = \frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}} \quad (20)$$

which gives the equilibrium contact angle in terms of the surface free energies of the three interfaces. This is a form of the Young–Dupré equation, originally stated in qualitative terms by Thomas Young in 1805, and in mathematical terms by Dupré in 1869.¹²

Alternatively, the Young–Dupré equation can be derived from mechanical arguments. Since the line of triple contact is subject to the tensions of three different surfaces, the vector resultant of these three tensions must vanish in the equilibrium situation.²² It is clear from Fig. 2 that Eq. (20) assures the equilibrium in the direction parallel to the plane solid surface but there is, however, a nonzero component normal to the plane. This means that no equilibrium situation can be achieved if the solid surface is plane in which case we must assume either that along the line of contact a local “puckering” of the solid surface occurs,^{13,14} or that no equilibrium condition is necessary for the normal components because the line of contact is not free to move in the normal direction.¹⁶ Some authors have proposed an adhesive force acting in the direction normal to the plane solid surface so as to maintain equilibrium,¹¹ but this is an unrealistic alternative and should be disregarded because this force is not a surface tension and its origin is unclear.

Finally, it should be noted that the normal component is not the only problem of this mechanical approach. The cases where $\Theta < 90^\circ$ are attributed to values of γ_{LS} smaller than γ_{SV} . When the mechanical approach is used, the student is given the impression that the solid–vapor interface plays a decisive role in determining the equilibrium shape of the drop,^{9,10} when in fact this equilibrium is actually determined by the intermolecular forces at the liquid–vapor and liquid–solid interfaces.

Capillary rise

In this third case study we deal again with three homogeneous phases in contact along three interfaces and a line of triple contact. In particular we consider a liquid column within a vertical cylindrical tube open to air in the upper end and immersed in a container of the liquid in the lower end (Fig. 3).

Having assumed the mass equilibrium between the three phases, the Helmholtz free energy of the system can now change due to a modification in the shape of the liquid–vapor interface and/or a change in the mass m of the liquid column. Thus, Eq. (12) must be modified to incorporate a new term accounting for the change in gravitational potential energy, $F_g = mgh_{c.m.}$, where $h_{c.m.}$ is the position of the center of mass of the liquid column with respect to the free surface

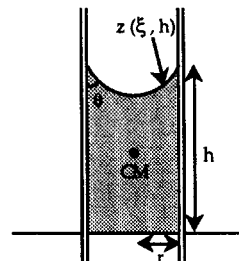


Fig. 3. Capillary rise in a vertical tube.

of the liquid in the container. The magnitudes m and $h_{c.m.}$ are taken as positive in the case of capillary rise and negative in the case of capillary depression, since both situations require positive gravitational energy.²⁵ First, let us remember that γ_{LV} is positive while $(\gamma_{LS} - \gamma_{SV})$ can be either positive or negative. If $\gamma_{LS} < \gamma_{SV}$ the liquid tends to wet the solid tube and the energy of the system is decreased by increasing A_{LS} , i.e., by producing a capillary rise effect. Of course, this rise is limited by the increase in gravitational energy, and a minimum free energy situation is eventually achieved. On the other hand, if $\gamma_{LS} > \gamma_{SV}$ the liquid tends to retreat from the solid walls and the energy of the system is decreased by decreasing A_{LS} , i.e., by producing a capillary depression. Again, this depression is limited by the increase in the gravitational energy. In addition, there is a tendency to flatten the liquid–vapor interface and reduce A_{LV} , but this tendency is usually buried by the tendency to wet (or retract from) the solid walls.

In this case, two conditions of mechanical equilibrium are needed: that of the liquid column and that of the line of triple contact. In order to derive them, we consider once again a spherical liquid–vapor surface of radius R , so that A_{LV} is given by Eq. (14). Also, if r is the radius of the cylindrical tube and h the height of the liquid in contact with the solid walls, the area of the liquid–solid interface is given by

$$A_{LS} = 2\pi r h. \quad (21)$$

Finally, we denote the angle of contact between the liquid–vapor and liquid–solid interfaces by θ (see Fig. 3), and its complement by Θ . Thus, $\theta = 0^\circ$ ($\Theta = 90^\circ$) in the case of a rising (wetting) hemispherical surface, $\theta = 90^\circ$ ($\Theta = 0^\circ$) if the surface is flat, and $\theta = 180^\circ$ ($\Theta = -90^\circ$) in the case of a retreating (nonwetting) hemispherical surface.

The condition of mechanical equilibrium of the line of triple contact can be obtained by considering changes in the contact angle, but not in the mass (volume) of liquid in the column. The change in the Helmholtz function is then

$$\begin{aligned} dF &= \gamma_{LV} dA_{LV} + (\gamma_{LS} - \gamma_{SV}) dA_{LS} + mg dh_{c.m.} \\ &= \gamma_{LV} 2\pi H dH + (\gamma_{LS} - \gamma_{SV}) 2\pi r dh \\ &= (\gamma_{LV} \cos \theta + \gamma_{LS} - \gamma_{SV}) 2\pi r dh = 0, \end{aligned} \quad (22)$$

where the change in gravitational energy has been neglected (since m is constant and only θ is changing), and we have made use of the condition

$$\begin{aligned} dm &= \rho d(\pi r^2 h - V) \\ &= \rho \left(\pi r^2 dh - \frac{\pi r}{\cos \theta} H dH \right) = 0 \quad (r \text{ fixed}). \end{aligned} \quad (23)$$

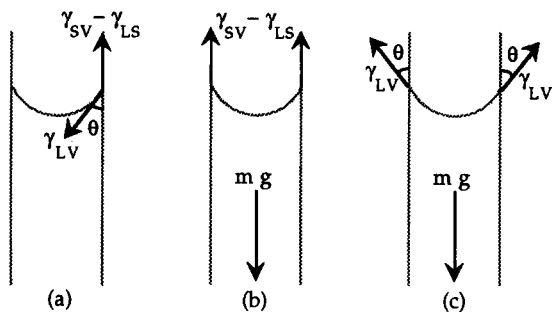


Fig. 4. Balance of forces in capillary rise: (a) equilibrium of the line of triple contact [Eq. (20)]; (b) equilibrium of the liquid column [Eq. (26)]; and (c) the situation usually depicted in physics textbooks [Eq. (28)].

Here, ρ denotes the density of the liquid, and the liquid column has been considered as a cylinder of radius r and height h minus a spherical cap of volume V given by Eq. (13) (see Fig. 3). Obviously Eq. (22) leads again to the Young–Dupré equation [see Eq. (20) and Figs. 2 and 3].

The condition of mechanical equilibrium of the liquid column is obtained by considering changes in the height of the column at constant contact angle θ . Thus, we have

$$dF = (\gamma_{LS} - \gamma_{SV})dA_{LS} + g d(mh_{c.m.}) \\ = (\gamma_{LS} - \gamma_{SV})2\pi r dh + mg dh = 0 \quad (24)$$

since

$$d(mh_{c.m.}) = \rho d \left(\int_0^r 2\pi \xi z \frac{z}{2} d\xi \right) \\ = \rho \int_0^r 2\pi \xi z dz d\xi = \rho dh \int_0^r 2\pi \xi z d\xi = m dh. \quad (25)$$

In Eq. (25), $z(\xi, h)$ denotes the equation of the liquid–vapor interface (i.e., ξ is an auxiliary variable measuring the distance from the column axis) and $dz = dh$ because θ is constant. Equation (24) now gives

$$(\gamma_{SV} - \gamma_{LS})2\pi r = mg \quad (26)$$

which implies the existence of capillary rise ($m > 0$) when $\gamma_{LS} < \gamma_{SV}$, and capillary depression ($m < 0$) when $\gamma_{LS} > \gamma_{SV}$. The equation for the capillary rise can also be written in the form

$$\frac{2\gamma_{LV} \cos \theta}{\rho g r} = \frac{2(\gamma_{SV} - \gamma_{LS})}{\rho g r} = h - \frac{V}{\pi r^2} \approx h. \quad (27)$$

Finally, we can give a mechanical interpretation of the above equations (see Fig. 4).²⁶ This interpretation can be done properly by considering that the forces involved are the surface tensions of the different interfaces, which act on the line of contact, and the weight of the liquid column. For instance, the force exerted by the liquid–vapor interface on the line of contact is $2\pi r \gamma_{LV}$ and acts along this interface, i.e., forming an angle θ with the solid walls. The equation for capillary rise is then obtained in two steps, just as in the thermodynamic approach. First, we consider the equilibrium of the line of triple contact, and obtain the Young–Dupré

equation. Second, we consider the liquid column, and state that the force exerted by the solid tube on the liquid column, $(\gamma_{SV} - \gamma_{LS})2\pi r$, must compensate for the weight of the liquid column mg , giving Eq. (26). The combination of these two results finally leads to Eq. (27).

However, the (mechanical) interpretation given in many textbooks^{1,3,11,21} differs from this: only γ_{LV} is invoked and the equilibrium is formulated (in a single step) as a balance between the weight of the liquid column and some force related to γ_{LV} . Most authors then introduce the force exerted by the solid walls on the liquid column as the reaction of the force exerted by the liquid–vapor interface on the line of contact. The vertical component of this reaction force is then said to cancel the weight of the liquid column, and the equation for capillary rise is written as

$$2\pi r \gamma_{LV} \cos \theta = \rho g \pi r^2 h. \quad (28)$$

Even though Eq. (28) is correct [see Eq. (27)], there are several weak points in this derivation. First, nothing is said about the physical magnitudes determining the value of the contact angle. Second, the student is left with the idea that capillary rise is directly related to γ_{LV} , while Fig. 4(b) and Eq. (26) state clearly that the force exerted by the solid walls on the liquid column is related to the difference in the surface tensions of the liquid–solid and solid–vapor interfaces. The direction of the force in Fig. 4(c) is also misleading, since the solid walls can only exert forces in the direction of the solid–liquid interface and not form an angle θ with it. Finally, the mechanical interpretation does not explain where the energy necessary for capillary rise comes from.¹⁴

CONCLUSIONS

Certainly, surface tension is not merely a “useful mathematical fiction” as suggested by many authors over the years (see, e.g., Ref. 9). The interfaces are under tension²⁷ and therefore surface phenomena can be readily explained, as in most physics textbooks, in terms of surface tension. However, only those few texts (see, e.g., Ref. 11) which define the surface tensions of the different interfaces, are able to give an acceptable explanation of capillary rise and the Young–Dupré equation.

In this paper, emphasis has been put on the surface free energy rather than on the surface tension not only because the surface free energy concept is considered to be more fundamental, but also because when the concept of surface tension is pushed too far, it leads to misleading results.⁹ In particular, the examples presented here (Young–Laplace and Young–Dupré equations, and capillary rise) have clearly shown a number of advantages of the thermodynamic approach to the study of elementary surface phenomena. (The main disadvantages of this approach are the complexity of the algebra and the need to introduce the Helmholtz function, which could mean that the formalism of thermodynamics could only be used in intermediate physics courses.) We conclude finally that: (i) thermodynamics and physical chemistry courses should favor the thermodynamic rather than the mechanical formalism when dealing with surface phenomena; and (ii) when the mechanical approach is still preferred, some weak points in the standard derivations (e.g., the existence of an adhesion force in the explanation of the Young–Dupré equation¹¹ and the nature and balance of forces in capillary rise) should be properly dealt with.

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Vibrational properties of a loaded string

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In this paper we discuss our study of a string-mass chain and its analogy to quantum mechanical systems. Theoretical predictions are made based upon the numerical solution to the wave equation. These predictions are tested experimentally using both normal mode analysis and pulse analysis. The frequency band structures for periodic and disordered string mass chains are studied as well as their corresponding eigenfunctions. The theoretical and experimental results are in accord. This experiment, suitable for advanced physics majors, demonstrates many important features of quantum mechanics: eigenvalues, superposition principle, band structure, gap modes, and Anderson localization. © 1995 American Association of Physics Teachers.

I. INTRODUCTION

The study of eigenstates and the corresponding eigenfunctions for periodic, quasiperiodic, and random systems has evolved from the Bloch periodic potential model to the Yablonoitch photonic crystal¹ and to Maynard's quasiperiodic, macroscopic models.^{2,3} In this paper we present theo-

retical models for periodic, quasiperiodic, and random string-mass chains and compare the theoretical model to our experimental results.

Periodic spring-mass and string-mass chains are extensively used as examples of eigenvalue problems because of the simplicity in mathematical treatment. For a string-mass chain, the mass of the string is usually assumed to be zero