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Simple measurement of surface free energy using a web cam

(Medida simples da energia livre de superfície usando uma web cam*)*

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Neste trabalho, descrevemos uma experiência simples e pedagógica para medir a energia livre de superfície (SFE) que é um tema dominante no ensino da Física, a nível de estudos de graduação e pós-graduação. A vantagem desta experiência baseia-se na simplicidade dos materiais utilizados, ou seja, produtos de baixo custo e não prejudiciais, como água, glicerol, etileno glicol e propanol, que oferecem uma boa oportunidade para discutir pedagogicamente conceitos básicos, mas relevantes sobre fenómenos de superfície. Como exemplo, medidas de ângulo de contacto foram utilizadas para estimar a SFE e a molhabilidade de diferentes superfícies sólidas, tais como o vidro e o politetrafluoretileno (PTFE, Teflon®).

Palavras-chave: práticas pedagógicas, energia livre de superfície, ângulo de contacto.

In this paper we describe a simple and pedagogical experiment to measure surface free energy (SFE), which is a mainstream subject to teach undergraduate and graduate level Physics science. Beyond this, the advantage of this work relies on the simplicity of the materials used, namely non-harmful and low cost products such as water, glycerol, ethylene glycol and propanol, offering a useful pedagogical opportunity to discuss basic but relevant concepts regarding surface science phenomena. As example, contact angle measurements were used to estimate SFE and the wetting behavior of distinct solid surfaces such as glass and polytetrafluoroethylene (PTFE, Teflon®).

Keywords: pedagogical practices, surface free energy, contact angle.

1. Introduction

Surface phenomena, namely surface free energy (SFE), is a multidisciplinary topic of interest at undergraduate and graduate levels, combining knowledge of physics, electrical engineering, materials science and thermodynamics. At a liquid-solid interface, the interaction forces are determined by the cohesion and adhesion forces. The ratio between these two forces permits the determination of the solids SFE. One way to experimentally determine the SFE of solids is the measurement of the contact angle between the outline surface tangent of a liquid drop and the surface [1-4]. The contact angle is a measure of a liquid ability to spread on a surface, which also enables the discrimination between polar and dispersive interactions.

In this work, a short review of the physical aspects that are involved in the contact angle measurements considering the "Owens and Wendt" method [5] is performed in section 2. Section 3 presents the experimental methodology to pedagogically implement contact angle measurements, using an accurate and very simple apparatus making using of non-harmful and cost effective liquid and solid materials, given emphasis to the apparatus implementation. In section 4, measurement of SFE will be pursuit by means of contact angle measurements of liquids on solid surfaces and the obtained results will be interpreted in terms of polar and dispersive contributions of the SFE and the wetting envelope function. At the end, final considerations about the developed method will be presented through the comparison of the obtained results with the ones in the literature.

2. Theoretical background

The contact angle is defined as the angle that a liquid drop surface makes when in contact with a solid surface. The contact angle value will depend on the liquid SFE and will initially vary with time as the liquid spreads

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over the surface. The wettability of a liquid on a solid surface is determined by the work of adhesion between the liquid and the solid, W_a, and the work of cohesion (defined as the work required to separate a unit area of two contacting phases), W_c, of the liquid. While the adhesive work contributes to the liquid spread over the solid surface, the cohesive one offers resistance to it, inducing a liquid contraction. The adhesive work and the cohesive work are related with the SFE of the liquid-vapour, γ_{LV}, solid-vapour, γ_{SV}, and solid-liquid, γ_{SL}, interfaces, according to Eqs. (1) and (2), respectively

$$W_a = \gamma_{LV} + \gamma_{SV} - \gamma_{SL} \tag{1}$$

$$W_c = 2.\gamma_{LV} \tag{2}$$

At equilibrium the energy must be stationary with respect to a shift of the solid-liquid boundary [6], Fig. 1, being given by Young's equation as function of the contact angle, θ

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cdot \cos(\theta). \tag{3}$$

From a thermodynamic point of view, when a liquid contacts a solid surface on the presence of a vapour phase, the liquid will wet the solid surface if the free energy value required to create a new surface is lower than the energy value of the liquid-vapour interface.

The equilibrium spreading coefficient, S, can be defined as the difference between the adhesion work W_a and the cohesion work W_c. The spreading parameter S is also defined as the difference between the SFE (per unit area) of the solid surface when dry and wet. For spontaneous spreading occurs it is necessary that the spreading coefficient S is negative, according to Eq. (4) [5].

$$S = W_a - W_c = [\gamma_{SV}]_{dry} - [\gamma_{LV} + \gamma_{SL}]_{wet}\,. \tag{4}$$

Owens and Wendt developed the idea that the SFE at a liquid-vapour and at a solid-vapour interfaces has two contributions, namely the polar (p) and the dispersive (d) ones, due to intermolecular interactions [5]. For a small vapour relative contribution, we may assume that $\gamma_{SV} = \gamma_S$ and $\gamma_{LV} = \gamma_L$.

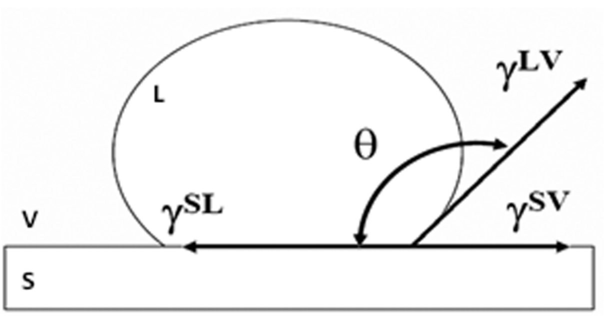

Figura 1 - Scheme representing the contact angle (θ) between the vapor (V), liquid (L) and solid (S) phases for a liquid on a solid surface.

Therefore, the SFE is composed of two components, the Lifshitz-van der Waals component (dispersive contribution, γ^d) and the dipoles and Lewis acid-base component (polar contribution, γ^p). The polar and dispersive contributions for the SFE can be express in the partial Eqs. (5) and (6) for liquids and solids, respectively

$$\gamma_L = \gamma_L^d + \gamma_L^p, \tag{5}$$

$$\gamma_S = \gamma_S^d + \gamma_S^p. \tag{6}$$

In pure liquids, the interaction between the liquid and the solid can be described in terms of reversible work of adhesion [5]

$$W_a = 2 \cdot \left(\sqrt{\left(\gamma_S^d \gamma_L^d\right)} + \sqrt{\left(\gamma_S^p \gamma_L^p\right)} \right). \tag{7}$$

From Eqs. (1), (3) and (7), results

$$\frac{\gamma_L\,(1+\cos(\theta))}{2\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p}\sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d}. \tag{8}$$

The previous linear relation written in terms of the independent variable $(\gamma_L^p/\gamma_L^d)^{1/2}$ and of the dependent variable $\gamma_L\,(1+\cos(\theta))\Big/2\sqrt{\gamma_L^d}$, allows us to determine the square root of the dispersive and polar solid SFE components.

When both dispersive and polar SFE are known, we can estimate which are the liquids that will wet the solid surface, through the so-called "wetting envelope" function [6]. The wetting envelope function calculation requires the numerical resolution of Eq. (8), replacing the values of the SFE components and the complete wetting condition (θ = *0*). In this case, a closed contour with a quadratic behavior is obtained in terms of the dispersive and polar components of the liquid. The knowledge of the solid wetting envelope enables easy wettability determination. Any liquid which polar and dispersive fractions lay within the contour will wet the corresponding solid surface [7].

3. Methodology

3.1. Experimental apparatus

Figure 2 shows a schematic representation of the implemented experimental apparatus constituted of a Web cam equipped with a CCD sensor (Creative® Live Ultra) to record videos with a minimum resolution of 640×480 pixels at 30 frames per second and of a diffuse light source made from a tungsten lamp. In our particular case, we connected it through an optical fiber array to render easier the redirection of the light into the liquid drop. A flat sample of the substrate material is placed underneath a syringe and a drop of liquid is dispensed onto the substrate. The syringe coupled with a needle of 0.5 mm diameter was used and manually handled to dispense a small liquid drop on substrates with minimum mechanical impact. The video of the drop deposition was acquired using the Arcsoft® Video Impression software that is provided with the web cam. The images of the liquid drop were extracted from the video files when a static condition of the drop shape was achieved.

The selected test liquids were water, glycerol, ethylene glycol and propanol with analytical-reagent quality, whose dispersive and polar components of the SFE are gather in Table 1 [7-9]. These values will be used to discuss the accuracy of the method proposed here.

The selected solid surfaces were sodalime Glass slides (Normax) and a thin sheet of polytetrafluorethylene (PTFE, Teflon®). The glass surface preparation includes three steps: glass slides were cleaned in an ultrasonic cleaner, with i) acetone during 15 minutes; ii) ethanol during 15 minutes and iii) dry at 60 °C during 10 minutes in an oven. The PTFE surface was cleaned with propanol in order to remove possible handling contaminations. The Glass and PTFE surfaces were cleaned under an air flux before the experimental measurements.

3.2. Experimental data analysis

The LB-ADSA (Low Bond Axisymmetric Drop Shape Analysis) program (`http://bigwww.epfl.ch/demo/dropanalysis/`) was used to fit the drop image profile and to measure the contact angle values. The LB-ADSA is based on the perturbation solution of the axisymmetric Laplace equation. It is thus suited to drops that are under the force of gravity on a horizontal substrate [10], as in the present case.

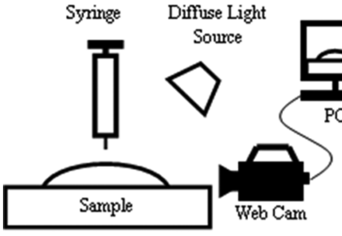

Figura 2 - Scheme of the experimental set-up used to acquire contact angles images.

Tabela 1 - Surface free energy dispersive (γ_L^d) and polar (γ_L^p) components (mN.m^{-1}) for selected contact angle test liquids at 24 °C.

	γ_L^d	γ_L^p
water [8]	21.8	51.0
glycerol [8]	34.0	30.0
propanol [9]	12.30	8.63
ethylene glycol [10]	30.9	17.4

4. Results and Discussion

Figure 3 exemplifies photographs of one drop of water, glycerol, propanol and ethylene glycol on the top of a PTFE surface.

For each liquid and solid surface 100 different measurements were performed so that the average contact angle is gathered in Table 2 for all the selected experimental conditions. For propanol deposited on glass, the contact angle values are very close to 0°, render difficult an accurate determination of the contact angle value, and therefore, were not consider in the calculation performed below. The fact that the contact angle value is $\sim 0°$, indicates a complete wetting of the surface.

In order to determine the dispersive and polar components of the surface energy for the Glass and for the PTFE solid surfaces, Eq. (8) was applied to the contact angle values in Table 2, yielding to the data in Fig. 4.

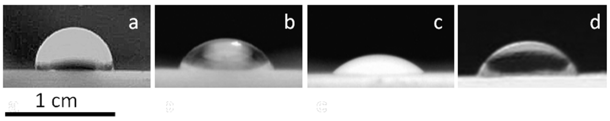

Figura 3 - Photographs of the drop of a) water, b) glycerol, c) propanol and d) ethylene glycol formed on the surface of PTFE.

Tabela 2 - Average contact angle values (°) measured for drops of water, glycerol, propanol and ethylene glycol formed on the top of PTFE and glass surfaces. The experimental errors are within 5%.

Surface	Test liquids			
	water	glycerol	propanol	ethylene glycol
PTFE	89.6	86.8	30.0	76.6
Glass	34.9	38.3	~ 0.0 °	35.1

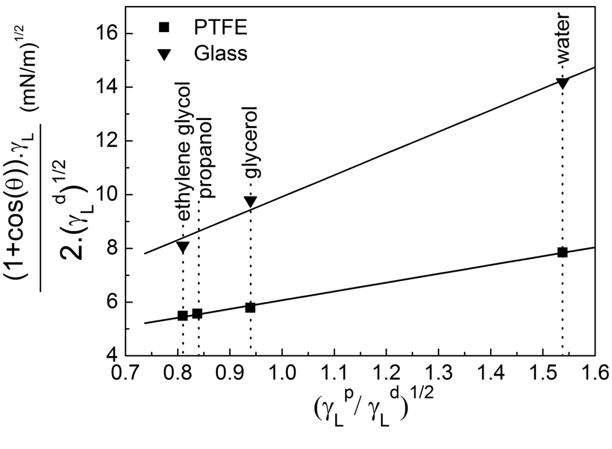

Figura 4 - Variation of the $\gamma_L(1+\cos(\theta))/2\sqrt{\gamma_L^d}$ dependent variable with the $(\gamma_L^p/\gamma_L^d)^{1/2}$ independent one for Glass and PTFE surfaces. The solid lines represent the data best linear fit ($r > 0.99$).

A linear dependence between $\gamma_L(1+\cos(\theta))/2\sqrt{\gamma_L^d}$ and $(\gamma_L^p/\gamma_L^d)^{1/2}$ was observed, enabling the determination of $\sqrt{\gamma_S^d}$ and $\sqrt{\gamma_S^p}$ values for each solid surface, using

Eq. (8). The linear fitting parameters, namely the slope (m) and intercept (b) were $m = 7.01 \pm 0.83$ and $b = 2.61 \pm 0.94$ (mN.m^{-1})$^{1/2}$ and $m = 2.79 \pm 0.13$ and $b = 3.28 \pm 0.12$ (mN.m^{-1})$^{1/2}$ for the Glass and the PTFE surfaces, respectively. The solid SFE values were calculated yielding to the results in Fig. 5. In order to validate the proposed methodology, the SFE values for Glass and PTFE reported in the literature [11, 12] are also shown in Fig. 5 for comparison purposes.

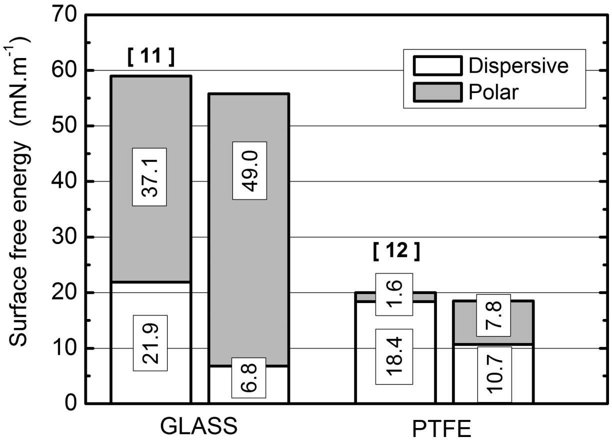

Figura 5 - Surface free energy values for Glass and PTFE. Data from the literature [11,12] is also included.

We can observe that the experimental results of SFE for Glass and PTFE obtained by this method are consistent with previous reported values [11, 12]. However, in the present study, polar contributions are more significant than that observed in previous studies [11, 12]. This difference can be ascribed to a less homogeneous surface of the substrates. The study of the surface roughness and non-homogeneity lies beyond the scope of the present work.

The knowledge of the contribution of the polar and dispersive SFE components allows the determination of the so-called surface wetting envelope. The polar and dispersive components of the liquid for which the contact angle is 0° are calculated and the polar fraction was plotted against the dispersive fraction, resulting in a closed contour which is called the wetting envelope. The calculated SFE values were used to determine the wetting envelope function of glass and Teflon® (Fig. 6). The envelope function describes the wetting of water, glycerol, ethylene glycol and propanol on the selected solid surfaces. All the used liquids have a partial wetting of the PTFE surface because the respective values of the SFE lie outside the PTFE closed contour. On glass, water and glycerol present a partial wetting, while propanol completely wets the glass surface with values lying within glass contour, as experimentally observed.

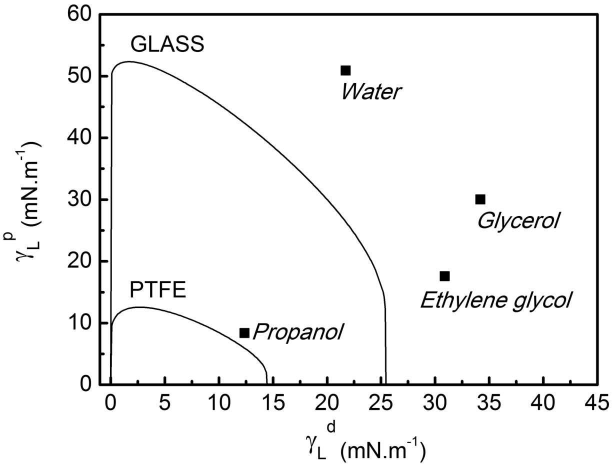

Figura 6 - Envelope functions for Glass and PTFE (solid lines). The squares represent the polar and disperse contributions of the surface free energy for selected liquids.

In general, solid surfaces with high values of SFE (constituted by covalent, ionic or metallic bonds) are completely wet by most of the liquids with low SFE, while solids with low SFE (bond by Van der Walls forces or in special cases, by hydrogen bonds) tend to be difficult wetted by those liquids, allowing only a partial wetting condition [13]. Some exceptions to this empirical rule were explained due the contribution of dispersion forces for the SFE [6].

In general, liquids such as water and alcohols (ethylene glycol, glycerol and propanol) have structural and dynamic properties that are influenced by intermolecular bonds namely hydrogen bond [14, 15]. The number of hydrogen bonds that a single liquid molecule can participate determinates the cohesion properties of liquids conditioning the SFE values [14]. This fact can be explained on a simplistic way by the different contact angle values and the liquids spreading tendency on a common substrate.

For PTFE and others fluorinated polymers it is well known that surface properties, in particular SFE, are related with weak molecular forces and the existence of C-F bonds from CF_2 groups [16, 17]. The properties of these surfaces depend not only on the coverage by the fluorocarbons but also on the degree of order of the surface [18, 19]. Moreover, glassy surfaces present a stronger polar character due to the existence of polar bonds that are responsible for a strong interaction with molecular groups of liquids, justifying its hydrophilic character [20].

5. Conclusion

In conclusion, we have presented a simple scheme to measure the contact angle between low cost and non-harmful liquid samples and distinct solid surfaces, which can be can be a useful pedagogical approach to study surface free energy related topics. The presented work stimulate discussion and allows an understanding of different properties resulting from a high surface free energy (Glass) and a low surface free energy (PTFE) solids, and how polar and dispersive components of surface free energy can determine wetting behavior of distinct surfaces. This example can be further used to stimulate discussion on the effects of the surface free energy in interactions at the interface.

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