Advances in Colloid and Interface Science xxx (2013) xxx–xxx

Contents lists available at ScienceDirect

Advances in Colloid and Interface Science

journal homepage: www.elsevier.com/locate/cis

Equilibrium contact angle or the most-stable contact angle?

F.J. Montes Ruiz-Cabello [a], M.A. Rodríguez-Valverde [b,*], M.A. Cabrerizo-Vílchez [b]

[a] Laboratory of Colloid and Surface Chemistry (LCSC), Department of Inorganic and Analytical Chemistry, University of Geneva, Switzerland
[b] Biocolloid and Fluid Physics Group, Department of Applied Physics, University of Granada, Campus de Fuentenueva, E-18071 Granada, Spain

ARTICLE INFO

Available online xxxx

Keywords:
Equilibrium contact angle
The most-stable configuration
Sessile drops
Mechanical vibration
Tilting

ABSTRACT

It is well-established that the equilibrium contact angle in a thermodynamic framework is an "unattainable" contact angle. Instead, the most-stable contact angle obtained from mechanical stimuli of the system is indeed experimentally accessible. Monitoring the susceptibility of a sessile drop to a mechanical stimulus enables to identify the most stable drop configuration within the practical range of contact angle hysteresis. Two different stimuli may be used with sessile drops: mechanical vibration and tilting. The most stable drop against vibration should reveal the changeless contact angle but against the gravity force, it should reveal the highest resistance to slide down. After the corresponding mechanical stimulus, once the excited drop configuration is examined, the focus will be on the contact angle of the initial drop configuration. This methodology needs to map significantly the static drop configurations with different stable contact angles. The most-stable contact angle, together with the advancing and receding contact angles, completes the description of physically realizable configurations of a solid–liquid system. Since the most-stable contact angle is energetically significant, it may be used in the Wenzel, Cassie or Cassie–Baxter equations accordingly or for the surface energy evaluation.

Contents

1. Introduction

A widely used approach for solid surface characterization is to measure the Advancing Contact Angle (ACA) and the Receding Contact Angle (RCA), which are associated with the amplitude of Contact Angle Hysteresis (CAH) [1]. Within the range of observable contact angles for a given solid–liquid system, ACA and RCA are the maximum and minimum stable values, respectively. On smooth solid surfaces, the ACA quantifies the low-surface energy domains (e.g. apolar surface groups) whereas the RCA is closely related to the high-surface energy domains (e.g. polar surface groups). Otherwise, on rough solid surfaces, the ACA also reveals the ascendant surface asperities, energetically favorable for the moving contact line, whereas the RCA is related to the descendent ones. However, ACA and RCA offer a scarce description of the surface energy and roughness degree of solid surfaces. Instead, a meaningful estimate of the mean wettability of solid–liquid systems is often necessary.

The evaluation of solid surface energies requires a contact angle related to the mean solid–liquid interfacial energy rather than the ACA and RCA [2]. In this text, the thermodynamically meaningful contact angle is referred as to the Equilibrium Contact Angle (ECA), although the precise term would be stable ECA. The term "equilibrium" can be confusing because it might be kinetically interpreted as the configuration where any drop dispensed over a surface should evolve to. In fact,

* Corresponding author. Tel.: +34 958 24 32 29; fax: +34 958 24 32 14.
E-mail address: marodri@ugr.es (M.A. Rodríguez-Valverde).

0001-8686/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cis.2013.09.003

any kinetically stable drop configuration between the advancing and receding configurations should be thermodynamically considered as a (meta)stable equilibrium configuration [3]. Otherwise, ECA will be the contact angle associated to the configuration of *global* minimum free energy of the system.

The global equilibrium configuration is hardly attainable in experiments and besides, it would be not readily recognizable [4]. Actually it is not possible to measure the energy of solid–liquid systems at different metastable configurations. Due to this, the definition of ECA is not operative. This also happens with the Young contact angle [5], which is experimentally inaccessible because it corresponds to the physically unrealizable model of ideal solid surface [6]. Unlike ECA, from a mechanistic point of view, we focus on the observable contact angle associated to the most stable equilibrium configuration of the system. The Most-Stable Contact Angle (MSCA) is the only measurable contact angle significantly connected to the (average) surface energy.

In this work, the current strategies for predicting the ECA are briefly reviewed. Next, the MSCA and its measurement based on mechanical stimuli are introduced. Two different stimuli are compared: mechanical vibration and tilting. Finally, we summarize the main findings and remarks.

2. Estimation of the equilibrium contact angle

The experimental determination of ECA is still an open question [7]. Firstly, it is often difficult to resolve whether the disagreement found in contact angle measurements reflects varying precisions of method, differences in techniques and experimental procedures or quality of the solid substrates [6,8–11]. Further, an important difficulty for measuring the ECA is the identification of the configuration of global minimum free energy. Whereas a sessile drop advancing or receding on the surface is at least optically recognizable, it is currently difficult to distinguish the drop with minimum free energy. In practice, the energy barriers (the energy difference between a local minimum and an adjacent local maximum) around the global minimum in the free energy curve are significantly high [12], and the system may remain "trapped" into an arbitrary metastable configuration close to the global equilibrium configuration. In fact, this experimental uncertainty is intrinsically associated to the CAH because certain stable values of contact angle are eventually observable but hardly measurable (repeatable). This just happens with the theoretical values of ACA and RCA [3,10]. In other respects, a solid–liquid–vapor system can be mechanically stable but far from the thermodynamic equilibrium because of the absence of diffusion equilibrium at common solid–liquid interfaces [13,14]. Besides, microscopic and molecular-scale deformations can occur on the solid surface to relax the unresolved vertical component of the liquid–vapor interfacial tension. Due to this, the rigorous mechanical equilibrium will be truly attained when the whole solid–liquid interface is accordingly deformed, as the Young modulus of the solid. Both thermodynamic and mechanical equilibrium conditions will be satisfied only on an *ideal* solid surface: smooth, chemically homogeneous, chemically inert and rigid surface; where the solid interfacial tensions numerically coincide with the respective specific interfacial energies. Hence, on moderately rigid solids and at experimental time scales, a mechanical equilibrium configuration is usually realized at the three-phase line rather than a global thermodynamic equilibrium state [15]. Finally, surface forces, such as disjoining/conjoining Derjaguin pressure, are also required to satisfy the condition of thermodynamic equilibrium of sessile drops [16].

Due to the operational inconsistency of the definition of ECA, this can be only estimated using observable contact angles. Several semi-empirical approaches have been suggested to predict ECA [7]. De Jonghe et al. [17] employed, on rough and chemically homogeneous surfaces, as estimate of ECA the arithmetic mean of the corresponding cosines of ACA and RCA. This approach, proposed by Good [18] from the mechanical equilibrium condition of the system, tends to be more accurate as the CAH decreases because it presumes that the system metastable configurations (observable contact angles) are symmetrically distributed around the global minimum energy. In general, the adhesion forces are not equal in magnitude over advancing and receding drops. If the ACA value is closer to the ECA value than the RCA one, the receding contact line will move with greater resistance. Only, when ACA and RCA are equidistant to ECA, the resistance to the contact line motion is equal in advancing and receding mode. Instead, Tadmor [19] proposed a weighted average based on the spherical cap approximation. Previously, Decker et al. [20] and Kamusewitz et al. [21] used the arithmetic mean of ACA and RCA instead of their cosines.

Rodríguez-Valverde et al. [22] modified the graphical method proposed by Schulze et al. [23] for rough surfaces, repeatedly used in literature [21,24,25]. This method is based on the plot of ACA and RCA in function of the difference of both angles, i.e. the amplitude of CAH, at different roughness degrees of the same solid surface. Fitting the ACA and RCA in terms of the hysteresis range enables to extrapolate the observed contact angle at zero hysteresis. Rodríguez-Valverde et al., from the Wenzel equation [26], used a nonlinear regression rather than the linear model of Schulze et al. based on simple geometric arguments [27], and the extrapolated value was assumed to be the ECA instead of the Young contact angle. These approaches assume that CAH is only caused by roughness. Actually, an atomically smooth surface can reveal CAH at certain scales, due to the scale-dependent heterogeneity. However, the individual effects of heterogeneity and roughness on contact angles cannot be separately analyzed. A residual hysteresis is always found at zero roughness-induced hysteresis [28].

As mentioned, the agreement between the values of ACA and RCA obtained with different techniques or measuring conditions is often complicated due to solid surface quality, interfacial geometry (meniscus, drop, bubble…), drop formation (handheld placed drop, growing captive drop, drop formed from below…), ambient/thermal vibration, optical resolution or signal sensitivity, numerical algorithm for contact angle evaluation, etc. Besides, the values of ACA and RCA on smooth polymer surfaces can become strongly dependent on the liquid and measuring method selected, as reported by Tavana et al. [29]. These authors concluded that the use of a function containing both ACA and RCA to estimate the solid surface energies is inappropriate, especially for polymer surfaces. Recently, Ruiz-Cabello et al. [30] suggested as meaningful contact angle (not ECA) the 'cross' arithmetic mean of the values of ACA and RCA provided by two methods: sessile drop and captive bubble methods. One 'cross' average was calculated from the value of ACA measured with the sessile drop method and the value of RCA measured with the captive bubble method, and vice versa for the reciprocal 'cross' average. Both values of 'cross' average agreed and this confirms that the 'cross' average quantifies indistinctly the dry and wetted states of the surface. Alike the ACA and RCA for inert solid surfaces, the cross-averaged angle and the CAH range were found to be representative of each polymer–liquid system, reflecting information about the liquid-substrate contact history.

3. The most-stable contact angle

In solid–liquid systems, instead of the global thermodynamic equilibrium configuration, the mechanically *most-stable* configuration is readily realizable. If a sessile drop were appropriately relaxed or stimulated (by mechanical vibration or inclination), from different initial metastable configurations, the most-stable configuration would be directly identified as the unaltered or less altered configuration. The excitation or stimulus should be sufficiently energetic to overcome the energy barriers between adjacent metastable configurations of the system, although over-relaxation effects are undesired. It is straightforward to understand this behavior from the metastability of a truncated cone (see Fig. 1). A truncated cone may be placed on a plane surface in different ways. Apart of the positions of unstable and neutral equilibrium, we focus on the stable equilibrium positions. The stable equilibrium

Please cite this article as: Ruiz-Cabello FJM, et al, Equilibrium contact angle or the most-stable contact angle?, Adv Colloid Interface Sci (2013), http://dx.doi.org/10.1016/j.cis.2013.09.003