Drops that pull themselves up

CrossMark

Rafael Tadmor

Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77710, United States

ARTICLE INFO

ABSTRACT

We relate different existing literature experimental findings of drop retraction in evaporating or in coffee ring systems as a unique physical phenomenon that is not related to evaporation, but rather to the presence of surfactant molecules in the drops. The retraction is induced by fluctuations of the drop's triple line that result in a net leakage of the surfactant molecules onto the solid-air interface right across the triple line. This net leakage can be induced by either nucleation and growth of a surface defect at the triple line or random triple line fluctuations analogous to spinodal process. Using this understanding, we can set a lower limit to the value of the, otherwise un-measurable, solid-vapor interfacial energy.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Retracting drops appear occasionally in various systems such as in coffee ring experiments [1] and other evaporation experiments [2,3], with ramifications to lab on a chip devices and DNA probes [4,5]. In evaporating systems in which the drops constantly contract, the retraction takes place together with the evaporation contraction and the two phenomena obscure each other. However, these are independent phenomena and retraction can be seen independently of evaporation (for example in case the surfactant and the entire drop are not volatile).

One example of a retracting system that is convoluted with evaporation is in the paper by Fang et al. [2] That paper establishes the evaporation problem theoretically as a function of physical constants of the evaporating liquid itself. Then the theory is strengthened by comparing it with various experimental systems which, despite having different evaporation patterns, all follow the same function of the liquid's physical constant. Two such systems that Fang et al. report have particularly unusual evaporation pattern (which nonetheless obeys their evaporation law): they exhibit drops retracting rather abruptly in the middle of the evaporation process. This happens for the systems of methanol drops as well as acetone drops, in both cases the substrate is octadecyltrichlorosilane treated silicon. Following the data points in the acetone case (for example), one can observe at least two consecutive jumps. Considering only the second (and bigger) jump, the drop moves within three seconds from 23° and almost 1 mm in diameter, to 66.5° and 0.37 mm (at t = 30 and 33 s respectively).

This corresponds to a transition from 38 nl to 7.5 nl and, despite the significant volume reduction, an ~20% increase in hydrostatic pressure [6] from 77 mPa to 94 mPa. Similar trends can be seen in other papers and other drop systems as presented in Fig. 1 for pure ethanol drop and a drop of a mixture of 70% ethanol and 30% water.

The examples above also exhibit a significant increase in the contact angle with respect to the initial contact angle of the system (which were 27° in (a) and (b) and 43° in (c)). The total increase in contact angle from its 'as placed' [6,7] value to the value at the end of the jumps sequence is even higher. For example in (c) it starts with 43° 'as placed' contact angle and at the retraction end reaches 89° [8–12].

The examples above, and a few other cases in these [2,3] and other [13] papers show drop systems that include surfactant molecules (or compose solely of them), that spontaneously increase their hydrostatic pressure at their triple line. Nonetheless, the triple line contracts to induce this change. Here, we address the mechanism of this phenomenon and the energy conservation problem that it seems to create. We show that the phenomenon is induced by a change in the solid-air interfacial tension. The retraction occurs with or without evaporation the two are non-related processes.

2. The retraction mechanism

A significant contact angle change represents a change in Young's equation:

$$\gamma_{SV} = \gamma_{SL} + \gamma \cos\theta_0 \qquad (1)$$

where γ_{SL}, γ, and γ_{SV} are the solid–liquid, liquid-vapor, and solid-vapor interfacial energies respectively, and θ_0 is the equilibrium contact angle

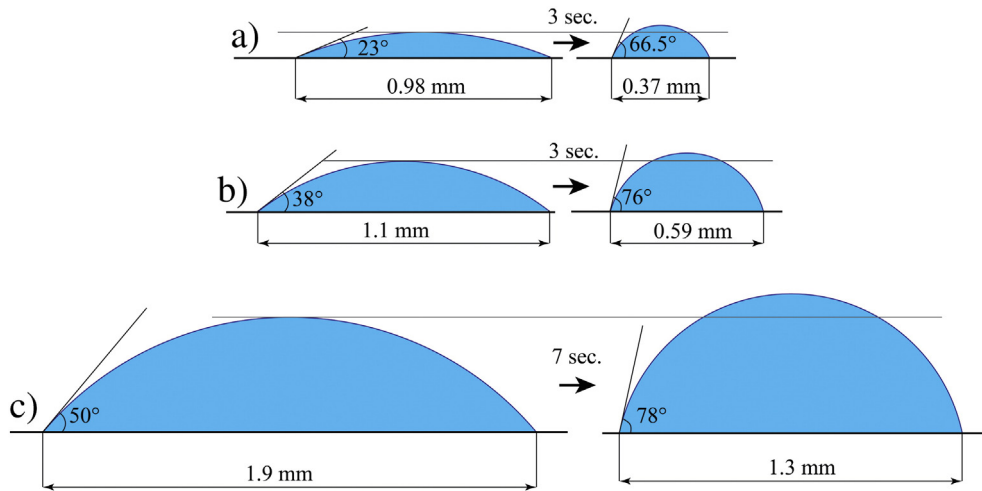*E-mail address:* Rafael.Tadmor@lamar.edu.

Fig. 1. Experimental data for spontaneous increase in the hydrostatic pressure. (a) acetone drop on octadecyltrichlorosilane treated silicon; (b) ethanol drop on octadecyltrichlorosilane treated silicon; (c) 70% ethanol and 30% water drop on octadecyltrichlorosilane treated silicon. Data taken from Fang et al. 2005 [2] for (a) and (b), and from Fang et al. 2009 [3] for (c). The gray horizontal lines provide references for the drops' heights increase.

that the drop makes with the solid. The Young equation is controlled by three interfacial energies, hence a change in it requires a change in one or more of these interfacial energies. Additionally, for a change to be energetically favorable, the system's energy needs to reduce.

We now consider the changes in the three interfacial energies: A reduction in the liquid-vapor interfacial energy, γ, or in the solid–liquid interfacial energy, γ_{SL}, (or both) corresponds to a decrease in the contact angle (the opposite of what we observe). However, a reduction in the solid-vapor interfacial tension increases the contact angle. Thus, of all interfacial tensions, the solid-vapor interfacial tension is the only candidate for a change that can explain retraction. Additionally, solid-vapor interfacial energy can indeed reduce if covered by surfactants.

Thus we conclude that retraction may occur if the system has two possible equilibrium contact angles that correspond to the two states represented in Fig. 2 and by Eqs. (2) and (3):

$$\gamma_{BA} = \gamma_{SL} + \gamma \cos\theta_S \tag{2}$$

$$\gamma_{SA} = \gamma_{SL} + \gamma \cos\theta_{RT} \tag{3}$$

where γ_{BA}, and γ_{SA} are the interfacial energies between the air and the bare solid (γ_{BA}), and between the air and the surfactant covered solid (γ_{SA}), and θ_S and θ_{RT} are the equilibrium contact angles of the drop at its maximal Spreading position, and at the minimal ReTraction position respectively as illustrated in Fig. 2. Note that γ_{BA} and γ_{SA} are specific names corresponding to two specific states of γ_{SV} (γ_{SV} being the general name for a solid-vapor interfacial energy).

When the drop touches the surface for the first time and spreads to reach its unsteady equilibrium contact angle, θ_S, the solid outside the drop is still deprived of surfactant and of high energy (and is therefore associated with a lower contact angle). The retraction transition is a transition from the quasi-equilibrium described in Eq. (2) to the equilibrium described in Eq. (3). Below we show that after some spreading time, fluctuations at the triple line expose the surfactant covered surface to the air and the system switches to the new and higher equilibrium contact angle, θ_{RT}.

3. Spinodal retraction vs. nucleation and growth

Eqs. (2)–(3) show why the retracting drop systems move from one thermodynamic equilibrium to the other. Each equilibrium corresponds
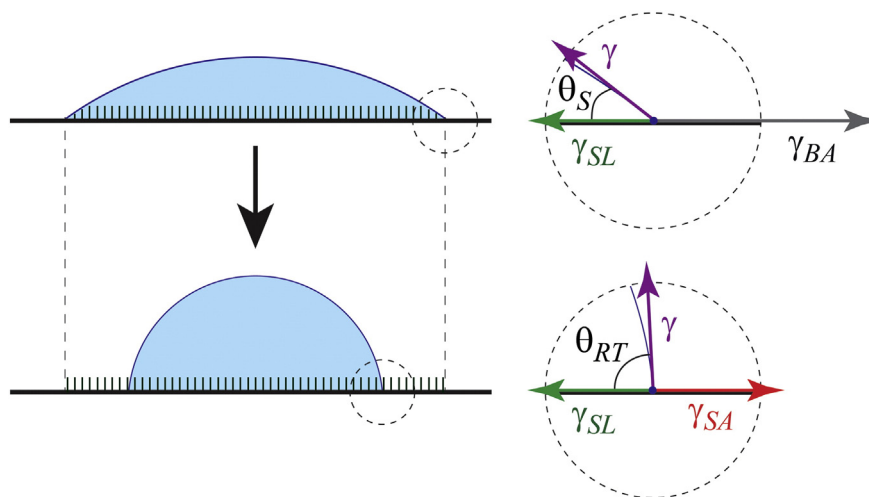

Fig. 2. Schematics of the two thermodynamic states the drop adapts. Top: Initially it adapts a lower contact angle, θ_S, toward an equilibrium with a bare solid-air interface of higher surface energy, γ_{BA}; this is an unsteady equilibrium. Bottom: Finally it adapts a higher contact angle, θ_{RT}, that corresponds to a steady equilibrium with surfactant covered solid-air interface, γ_{SA}. Left: Schematics of the drop and surfactant before and after the retraction; Right: The vectorial representation of the surface tensions according to the left images and Eqs. (2) and (3). Note that the only change is in γ_{SV} which changes its value from γ_{BA} to γ_{SA}.