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Asymmetric capillary bridges between contacting spheres

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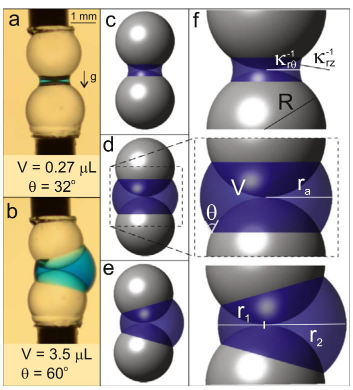
GRAPHICAL ABSTRACT



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ABSTRACT

When a drop of liquid wets two identical solid spheres, the liquid forms a capillary bridge between the spheres to minimize surface energy. In the absence of external forces, these bridges are typically assumed to be axisymmetric, and the shape that minimizes surface energy can be calculated analytically. However under certain conditions, the bridge is axisymmetrically unstable, and migrates to a non-axisymmetric configuration. The goal of this paper is to characterize these non-axisymmetric capillary bridges. Specifically, we numerically calculate the shape of the capillary bridge between two contacting spheres that minimizes the total surface energy for a given volume and contact angle and compare to experiments. When the bridge is asymmetric, finite element calculations demonstrate that the shape of the bridge is spherical. In general, the bridge shape depends on both volume and contact angle, yet we find the degree of asymmetry is controlled by a single parameter.

1. Introduction

When a small amount of liquid wets two identical solid spheres, the liquid will typically form a meniscus, or capillary bridge, between the spheres. Provided that bridge is sufficiently small, gravitational effects are negligible, and the liquid is drawn to the axis of the spheres to minimize surface energy. Extensive research has been carried out to characterize capillary bridges, both because of the elegance of the mathematics [1,2] and because of their importance to a variety of processes in physics and engineering [3–6]. Capillary bridges are important to granular and suspension rheology [7,8]. They trap liquids and gases in soil [9,10] and porous rock [11], as well as influence the adhesion of pharmaceutical powders [12] and sandcastles [13,14]. Yet, almost all studies of capillary bridges between spheres have restricted their analysis to situations in which the bridges are axisymmetric [15–21]. Of the few studies that have pointed out the existence of asymmetric

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capillary bridges between spherical particles [22,23], there is an indication that these bridges might adopt a spherical shape; yet the authors were careful not to claim that the asymmetrical spherical bridge indeed minimized surface energy.

The shape of both an axisymmetric and non-axisymmetric capillary bridge can be demonstrated experimentally (Fig. 1a and b). Two glass spheres are adhered to needles and brought to contact. Water, dyed blue, is injected on the spheres and forms a capillary bridge between the spheres and the surrounding air. An axisymmetric capillary bridge forms between the spheres (radius $R = 1$ mm) when the water volume is $V = 0.27$ μL and the apparent contact angle is $\theta = 32°$ (Fig. 1a). As will be described further in the method's section, the particular contact angle is achieved by vapor-depositing a layer of (3-mercatopropyl)trimethoxysilane onto the glass spheres prior to assembly. Above a critical drop volume and apparent contact angle, however, the capillary bridge spontaneously breaks axial symmetry and bulges to one side (Fig. 1b). The goal of this paper is to numerically calculate the shape of bridges that minimize the surface energy for various combinations of volume and contact angle.

In the absence of external forces, the liquid bridge will rearrange until it locally minimizes the cumulative surface energy of each of the interfaces. When a liquid, gas, and solid phase are present, the total surface energy can be expressed as $E = \gamma_{LG}A_{LG} + \gamma_{SG}A_{SG} + \gamma_{SL}A_{SL}$, as there are three distinct interfaces (liquid–gas, solid–gas, and solid–liquid) each with their own interfacial tension γ and surface area A. In the absence of any roughness or chemical heterogeneities, the relative strengths of the surface energies manifest themselves through the equilibrium contact angle θ_{eq} that the three phases make when they meet, following Young's relation [4]: $(\gamma_{SG} - \gamma_{SL})/\gamma_{LG} = \cos\,\theta_{eq}$. In practice, microscopic heterogeneities can be significant and the angle

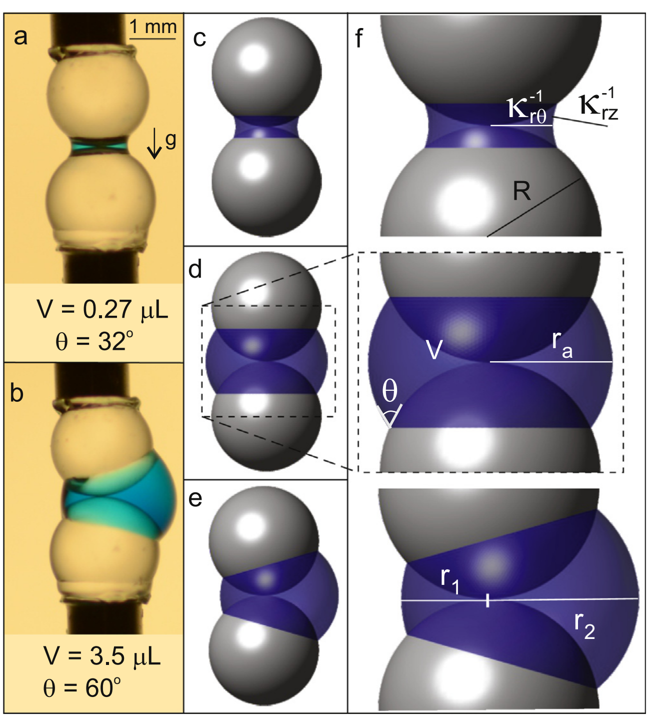

Fig. 1. Experiments and simulations illustrating axisymmetric and asymmetric morphologies. (a) A photograph of 0.27 μL of water wetting two glass spheres with contact angle $\theta = 32°$. (b) At an increased volume ($V = 3.5$ μL) and contact angle ($\theta = 60°$), the water adopts a non-axisymmetric topology. (c) Minimal energy surface simulated for conditions in part a. (d) Axisymmetric minimal energy surface simulated for conditions in part b. (e) Stable minimal energy surface simulated for conditions in part b. (f) Identification of parameters measured from the simulations.

macroscopically observed, referred to here as the apparent contact angle, can deviate from the equilibrium value [24,25]. In addition, the apparent contact angle can modulate between values adopted when the contact line is quasi-statically receding and when the contact line is quasi-statically advancing, a phenomenon referred to as contact angle hysteresis [26,27]. Although the experimental system in Fig. 1 exhibits contact angle hysteresis, the analysis in this paper demonstrates that hysteresis is not necessary to adopt an asymmetric capillary bridge. In this paper, we will refer to the fluid that forms the capillary bridge as a liquid and the surrounding fluid as a gas to be consistent with Fig. 1. However, it should be noted that the analysis presented here does not restrict these phases to be liquid and gas respectively, but rather generalizes to any two immiscible fluids.

The topological transition illustrated in Fig. 1a and b is reminiscent of the non-axisymmetric instability observed when a drop is squeezed between two parallel disks [28–30]. In that scenario, the capillary bridge adopts a rotund shape and breaks symmetry when the free surface is tangent to the flat surface of the disk. Yet, the contact line on the parallel disks is pinned, whereas on the spheres we will assume that it is free to move along the surface.

Therefore, a closer analogy to the shape transition (Fig. 1a and b) might be the roll-up process of a drop on a cylinder [31–35]. Depending on the contact angle and the volume, a drop will spread around a long cylinder in a shape resembling a barrel shape or alternatively roll-up into a non-axisymmetric shape resembling a clamshell. The drop and cylinder geometries provide a seemingly simple system; yet, even though the morphologies have been calculated numerically [33–35], the precise instability criterion and non-axisymmetric topology are still uncertain [35]. A challenge is the existence of metastable states in which a drop can conform to a topology that is a local energy minimum while not necessarily being a global minimum. The double-sphere geometry (Fig. 1) may be a simpler system to characterize non-axisymmetric bridge morphologies due to rotational symmetries. Yet, as far as we are aware, the stable, non-axisymmetric topologies for drops on the double-sphere geometry have not been calculated analytically or numerically.

In the following sections, we describe our procedure to model the capillary bridge between identical spheres both experimentally (Fig. 1a and b) and numerically (Fig. 1c–e) for a given liquid volume V and contact angle θ. From the finite element calculations, we measure the principle curvatures κ_{rz} and $\kappa_{r\theta}$, as well as the minimum r_1 and maximum r_2 extent of the bridge from the point of contact (Fig. 1f). These parameters are collected for various combinations of volume and contact angle and form the basis of our analysis.

2. Methods

2.1. Experimental methods

To obtain the images in Fig. 1a and b, borosilicate glass beads with a diameter of 2 mm are adhered to the tip of 16 gauge needles. The beads are coated with (3-mercatopropyl) trimethoxysilane by chemical vapor deposition under low pressure so that they are partially wetting. Once coated, the needles are mounted vertically so that the glass beads can be aligned and brought into contact by articulating a 3D stage. Water, dyed blue, is injected between to form a capillary bridge between the separated spheres.

For small volumes, the capillary bridge remains axisymmetric when the glass beads are brought into contact. In these cases only a single photograph is taken. For larger volumes, however, the bridge becomes non-axisymmetric as the beads are drawn together. In these cases, a second photo is taken while the beads