Shape instabilities of particle-covered collapsing droplets

Sonia Melle[*,†], Gerald G. Fuller
Dpto. de Optica, Universidad Complutense de Madrid, Ciudad Universitaria s/n, 28040 Madrid, Spain
Department of Chemical Engineering, Stanford University, Stanford, CA 94305-5025

The behavior of colloidal particles confined to the interface between two different liquid phases is of particular interest as they serve as a model system to study crystallization processes[1,2], and is also significant for their industrial applications as, for example, the stabilization of the so-called Pickering emulsions[3,4]. An important process that occurs with emulsions is desiccation or drying. This can occur with either drops attached to surfaces in the form of pendant or sessile drops, or suspending in air, as in the case of spray drying. The majority of previous studies on the collapse of droplets have considered the problem of desiccation[5,6], and have reported on remarkable shape transitions by evaporating droplets composed of complex liquids consisting of polymer solutions or particulate suspensions.

It is well-known that a liquid droplet immersed in another fluid, i.e., encapsulated by a "clean" interface that is only characterized by a surface tension γ, will be reduced in size in a manner that is completely described by the Young-Laplace equation, $\Delta p = \gamma C$, where $\Delta p = p_i - p_o$ is the pressure difference (in-out), and $C = {R_1}^{-1} + {R_2}^{-1}$ is the curvature of the surface, with R_i the radii of curvature. In the absence of gravity, a suspended droplet will remain spherical, and the internal pressure, p_i, will increase in inverse proportion to the decreasing drop radius ($R = R_1 = R_2$). If the droplet is sessile, it will shrink as a spherical cap and its contact angle will remain constant. However, the situation is completely changed if the droplet contains suspended particles, which can be driven to the interface. This can induce a transition from an interface that is fluid and only characterized by a surface tension towards a solid film that possesses elastic moduli and that can sustain anisotropic stresses.

We have studied a system formed by a sessile droplet of water adhered to a Delrin surface which is drained from below. The droplet is surrounded by decane and covered with a monolayer of polystyrene particles with a diameter of 3 μm. In this system the transition from a fluid film to a solid film is manifested in shape transitions and buckling of the droplet as its volume is decreased. The initial coverage of particles is sufficiently low to create an interface that is very fluid. However, at some point during the drainage of the droplet, the particles approach one another and cause the droplet surface to become a solid shell. At this moment, the buckling of the shell produces a flattened, circular disk that proceeds downward (see Figure 1). This disk shows a crumpled topology with undulations that are roughly in the form of concentric, annular ridges. The number of ridges increases until the droplet finally collapses. By modelling this problem as analogous to the buckling of an elastic beam[7,8], we can estimate the Young's modulus of these particle monolayers through the measurement of the wavelength of these instabilities.

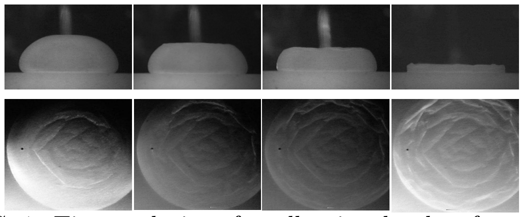

FIG. 1. Time evolution of a collapsing droplet of water surrounded by decane. The interface is covered with polystyrene particles of 3 μm in diameter. On top is the side view. At bottom is the top view.

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[*] smelle@fis.ucm.es
[†] `http://www.ucm.es/info/mclab`

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