Interpretation of elasticity of liquid marbles

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HIGHLIGHTS

- Liquid marbles are non-stick droplets covered with micro-scaled particles.
- Liquid marbles demonstrate quasi-elastic properties when pressed.
- The interpretation of the phenomenon of elasticity of liquid marbles is proposed.
- The growth in the surface in the course of deformation explains elastic properties of marbles.

GRAPHICAL ABSTRACT

Polyethylene coated 10 µL liquid marble.
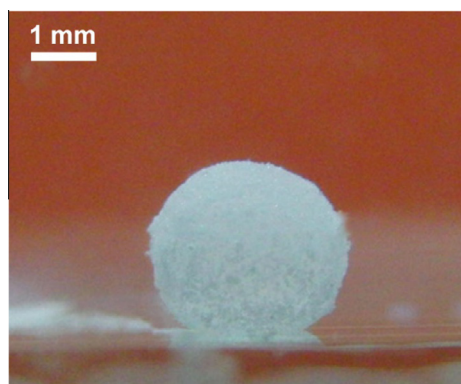
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ABSTRACT

Liquid marbles are non-stick droplets covered with micro-scaled particles. Liquid marbles demonstrate quasi-elastic properties when pressed. The interpretation of the phenomenon of elasticity of liquid marbles is proposed. The model considering the growth in the marble surface in the course of deformation under the conservation of marble's volume explains semi-quantitatively the elastic properties of marbles in satisfactory agreement with the reported experimental data. The estimation of the effective Young modulus of marbles and its dependence on the marble volume are reported.

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1. Introduction

Liquid marbles are continuing to draw the attention of investigators [1–4]. Liquid marble, shown in Fig. 1, is the non-stick droplet encapsulated with micro- or nano-scaled solid particles [5–7]. Since liquid marbles were introduced in the pioneering works of Quèrè et al., they have been exposed to the intensive theoretical and experimental research [8–13]. An interest in liquid marbles arises from both their very unusual physical properties and their promising applications. Liquid marbles present an alternate approach to superhydrophobicity, i.e. creating a non-stick situation for a liquid/solid pair. Usually superhydrophobicity is achieved by a surface modification of a solid substrate. In the case of liquid marbles, the approach is opposite: the surface of a liquid is coated by particles, which may be more or less hydrophobic [13]. Marbles coated by graphite and carbon black, which are not strongly hydrophobic, were also reported [14,15].

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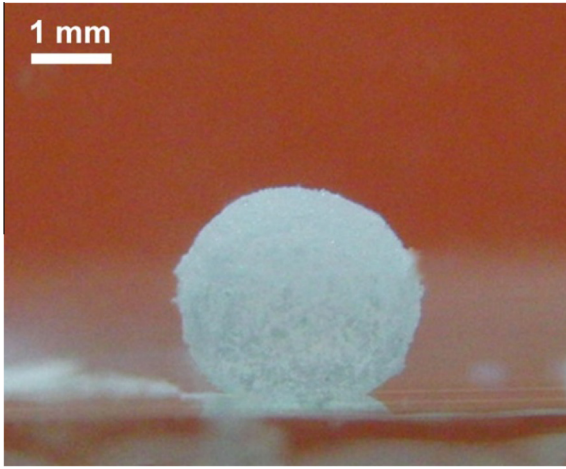*E-mail address:* edward@ariel.ac.il (E. Bormashenko).

Fig. 1. Typical 10 μL water marble coated by polyethylene particles.

A variety of media, including organic and ionic liquids and liquid metals, could be converted into liquid marbles [16–18]. Liquid marbles were successfully exploited for microfluidics [1,4,18–21], water pollution detection [22], gas sensing [23], blood typing [24] and optical probing [25]. Respirable liquid marbles for the cultivation of microorganisms and Daniel cells based on liquid marbles were reported recently by Shen et al. [26,27]. Stimulus (pH, UV and IR) responsive liquid marbles were reported by Dupin, Fujii et al. [28–30]. It is noteworthy that liquid marbles retain non-stick properties on a broad diversity of solid and liquid supports [31]. Actually, liquid marbles are separated from the support by air cushions in a way similar to Leidenfrost droplets [32]. The state-of-the-art in the study of properties and applications of liquid marbles is covered in recent reviews [33–36].

Remarkably, liquid marbles demonstrate certain elastic properties and can sustain a reversible deformation of up to 60% [37]. Our paper is devoted to elucidating elastic properties of liquid marbles.

2. The model

We relate the stress, arising from deformation of the marble, to the growth of its surface energy due to the area increase. We accept a simple model, approximating the shape of the deformed marble by a symmetrical spherical segment, and take into account the conservation of marble volume, $V = V_0$, in the course of deformation:

$$V = \frac{4}{3}\pi R^3 - \frac{2}{3}h^2(3R - h), \quad V_0 = \frac{4}{3}\pi R_0^3, \tag{1}$$
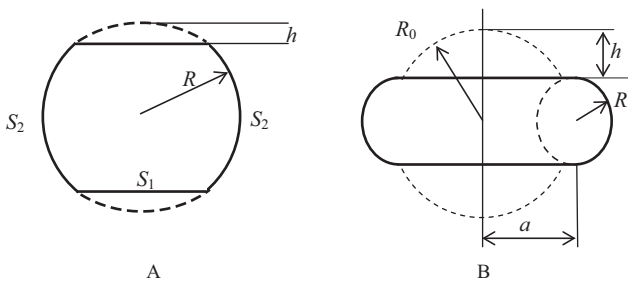

Fig. 2. (A) The model of the deformed marble presented as a symmetric spherical segment. The upper and lower circles, which arise as a result of the equal deformations h, have the same area S_1. The side area of the spherical segment is S_2. In the course of deformation, the radius R increases, but the segment volume is conserved. (B) The "pancake" model of the strongly deformed marble.

where R_0 and R are the radii of non-deformed and deformed marbles, respectively, and h is the deformation (see Fig. 2A). The deformations of the spherical marble from above and from below are supposed to be equal. Thus, the influence of its weight is neglected that is a reasonable simplification for small marbles, when the radius of a marble is smaller than the so-called capillary length, $l_{ca} = \sqrt{\gamma_{eff}/\rho g}$ and γ_{eff} is the effective surface tension of a marble [10]; ρ is its density. The effective surface tension of liquid marbles is not single-valued due to its pronounced hysteretic nature [10]; however, for a sake of a very rough approximation a value of $\gamma_{eff} \cong 60-70$ mN/m may be assumed. Thus the value of the capillary length is $l_{ca} \cong 2.5$ mm for various kinds of coating powders.

The requirement of conservation of volume dictates the following expansion of R in terms of powers of h up to the fourth order

$$R \approx R_0 + \frac{1}{2R_0}h^2 - \frac{1}{6R_0^2}h^3 + O(h^5). \tag{2}$$

Note the absence of the first and fourth powers of h from expansion (2). The overall area of the upper and lower circles is, on account of (2)

$$2S_1 = 2\pi(2Rh - h^2) \approx 2\pi\left(2R_0h - h^2 + \frac{1}{R_0}h^3 - \frac{1}{3R_0^2}h^4\right). \tag{3}$$

In the same approximation, the side area of the spherical segment is

$$S_2 = 4\pi R^2 - 4\pi Rh \approx 4\pi\left(R_0^2 - R_0h + h^2 - \frac{5}{6R_0}h^3 + \frac{5}{12R_0^2}h^4\right). \tag{4}$$

The overall increase in the surface area takes a form

$$\Delta S = 2S_1 + S_2 - 4\pi R_0^2 \approx 4\pi\left(\frac{1}{2}h^2 - \frac{1}{3R_0}h^3 + \frac{1}{4R_0^2}h^4\right). \tag{5}$$

The increase in the area under deformation induces the increase in the surface energy of the marble, $\Delta E = \gamma\Delta S$ and the corresponding elastic force is:

$$F = \frac{d\Delta E}{dh} \approx 4\pi\gamma_{eff}\left(h - \frac{1}{R_0}h^2 + \frac{1}{R_0^2}h^3\right). \tag{6}$$

where γ_{eff} is the effective surface tension of the composite marble surface. A characteristic feature of this elastic force is the inflection, $d^2F/dh^2 = 0$, at

$$h = \frac{1}{3}R_0. \tag{7}$$

It is latently assumed, that γ_{eff} does not change in a course of deformation. Proceeding from Eq. (6), the stress–strain dependence is determined as:

$$\sigma = \frac{4\gamma_{eff}}{R_0}\left(\varepsilon - \varepsilon^2 + \varepsilon^3\right). \tag{8}$$

where $\sigma = \frac{F}{\pi R_0^2}$ and $\varepsilon = \frac{h}{R_0}$.

Surprisingly, all the coefficients at the powers of h came out the same. Note the unusual even power of strain in (8) that reflects the asymmetry in pressing and stretching liquid marbles. Even if the stretching were possible experimentally, the marble would turn under stretching into a body resembling a prolate spheroid (not a spherical segment like that in Fig. 1) with a different dependence of the surface area on the deformation h. Expression (8) also predicts a weak inverse dependence of stress on the marble volume (as the inverse of the cubic root), as well as the Young modulus in a linear approximation

$$E \approx \frac{4\gamma_{eff}}{R_0}. \tag{9}$$