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Pendant capsule elastometry

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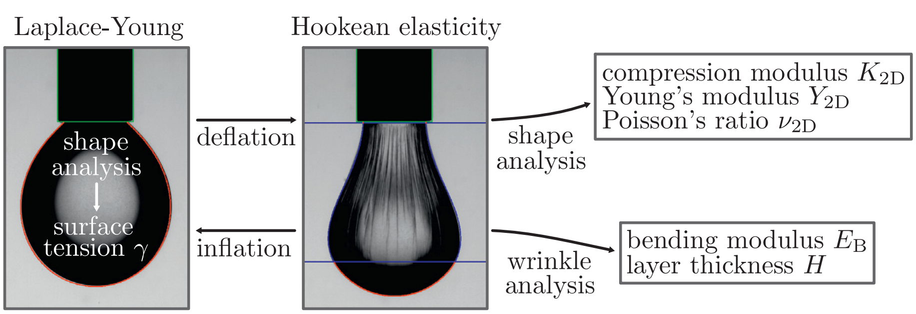
GRAPHICAL ABSTRACT



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ABSTRACT

We provide a C/C++ software for the shape analysis of deflated elastic capsules in a pendant capsule geometry, which is based on an elastic description of the capsule material as a quasi two-dimensional elastic membrane using shell theory. Pendant capsule elastometry provides a new in situ and non-contact method for interfacial rheology of elastic capsules that goes beyond determination of the Gibbs- or dilational modulus from area-dependent measurements of the surface tension using pendant drop tensiometry, which can only give a rough estimate of the elastic capsule properties as they are based on a purely liquid interface model. Given an elastic model of the capsule membrane, pendant capsule elastometry determines optimal elastic moduli by fitting numerically generated axisymmetric shapes optimally to an experimental image. For each digitized image of a deflated capsule elastic moduli can be determined, if another image of its undeformed reference shape is provided. Within this paper, we focus on nonlinear Hookean elasticity because of its low computational cost and its wide applicability, but also discuss and implement alternative constitutive laws. For Hookean elasticity, Young's surface modulus (or, alternatively, area compression modulus) and Poisson's ratio are determined; for Mooney-Rivlin elasticity, the Rivlin modulus and a dimensionless shape parameter are determined; for neo-Hookean elasticity, only the Rivlin modulus is determined, using a fixed dimensionless shape parameter. Comparing results for different models we find that nonlinear Hookean elasticity is adequate for most capsules. If series of images are available, these moduli can be evaluated as a function of the capsule volume to analyze hysteresis or aging effects depending on the deformation history or to detect viscoelastic effects for different volume change rates. An additional wrinkling wavelength measurement allows the user to determine the bending modulus, from which the layer thickness can be derived. We verify the method by analyzing several materials, compare the results to available rheological measurements, and review several applications. We make the software available under the GPL license at github.com/jhegemann/opencapsule.

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1. Introduction

Elastic capsules that consist of a solid thin shell enclosing a liquid volume can be produced artificially by a variety of chemical processes, such as interfacial crosslinking or polymerization [1]. Moreover, solid-like interfaces can form by interfacial adsorption and self-assembly of surface active micro- or nano-particles such as colloidal particles in colloidosomes [2], petroleum [3], various proteins at interfaces [4,5], for example hydrophobins at water-air interfaces [6]. Eventually, solid-like shells can likewise be formed using layer-by-layer assembly by employing electrostatic interactions of polyelectrolytes [7–9]. Elastic capsules have many applications for transport and delivery of the enclosed liquid in pharmaceutical, cosmetic or chemical industry [10]. Likewise, they serve as biological model systems for red blood cells or the cell cortex. For all applications, a characterization of the mechanical properties of the capsule shell, i.e., its elastic moduli, is necessary [11,10].

Encapsulation applications employ closed microcapsules, but often capsules can likewise be produced in a pendant or hanging capsule geometry, where the capsule is not closed and the capsule edge is attached to a capillary [12–16,6,17,18,9]. Such capsules can be produced by self-assembly onto a droplet hanging from a capillary or onto an air bubble rising from a capillary, or by interfacial crosslinking at the interface of a pendant droplet [19]. An advantage of this pendant capsule geometry is that volume reduction or pressure application can easily be realized by fluid suction through the capillary and it, thus, offers a simple way of micromanipulation for mechanical characterization.

The related pendant droplet tensiometry is a standard tool to determine the surface tension of a liquid interface using the Laplace-Young equation to model the droplet shape [20–23], which is commercially available. The same Laplace-Young analysis has frequently been applied to pendant elastic capsules with different shell materials or droplets coated with solid-like layers of adsorbed particles [3,24,8,12,25,26,4,15–17] resulting in the determination of an "effective surface tension" γ describing the solid shell interface of surface area A. Changing the surface area A in deflation experiments, the so-called Gibbs- or dilational modulus $E_{\text{Gibbs}} = d\gamma/d\ln A$ can be calculated. Pendant drop tensiometry can also be applied to droplets or capsules with a viscoelastic interface by employing oscillating droplets [24,12,25,26,4]; then a complex dilational modulus can be obtained, which includes a real elastic and an imaginary loss part. The elastic dilational modulus is equal to the area compression modulus K_{2D} for a fluid interface or for a two-dimensional solid interface in a planar Langmuir-Blodgett trough geometry. Application of the same concept to pendant elastic capsules gives misleading results because of inhomogeneous and anisotropic elastic stresses in the capsule geometry and the existence of a curved undeformed reference shape of the capsule [12–14,19,9]. In Ref. [19], an elastic model based on shell theory has been developed which is capable of describing capsule shapes in a deflation experiment more realistically. Similar elastic models have been formulated in Refs. [12–14,9]. In Ref. [19] this approach has been extended to the pendant capsule elastometry method, where the elastic model is used to determine two elastic constants, the surface Young modulus Y_{2D} and Poisson's ratio ν_{2D}, by optimally fitting calculated shapes to experimental images. Pendant capsule elastometry has already been applied to OTS-capsules and hydrophobin-coated bubbles [19] but also to bacterial films at interfaces [27].

Here, we want to present and make publicly available a much more efficient implementation of the pendant capsule elastometry method as a C/C++ software with a high degree of numerical efficiency and automation. In contrast to Ref. [19], where elastic constants were optimized on a grid in parameter space to optimally match the experimental shape profile, we optimize elastic constants in continuous parameter space, which improves both performance and accuracy. Moreover, we go beyond Ref. [19] and generalize the shape analysis method to other constitutive laws. In particular we investigate the behavior of the shape analysis method in combination with Mooney-Rivlin or neo-Hookean elasticity models, which are commonly used for inextensible polymeric materials.

These significant improvements turn the analysis into a strong tool to investigate different materials in a short time and on a large scale. We demonstrate these capabilities by analyzing a variety of deformation experiments for different materials. In pendant capsule elastometry Young's modulus and Poisson's ratio (or the Rivlin modulus and the dimensionless shape parameter) of the two-dimensional capsule shell material are obtained from an analysis of a digitized image of the deflated capsule shape and a second image of its undeformed reference shape. If the capsule wrinkles upon deflation, an additional wrinkling wavelength measurement allows us to determine the bending modulus, from which the layer thickness can be derived if the shell material is a thin layer of a three-dimensional isotropic elastic material.

2. Available experimental methods

Several interfacial rheology methods exist, which allow the determination of the elastic properties of the capsule shell material. We review four different rheological methods, which we will use as references for the pendant capsule method described in this paper. Typical experimental methods are (i) surface shear-rheometry [28], (ii) Langmuir-Blodgett trough, (iii) shear flow rheoscope (flow cell) [29], and (iv) spinning drop apparatus [30]. Methods (i) and (ii) work with *planar* membranes of the shell material, whereas methods (iii) and (iv) directly work in the curved capsule geometry, like pendant capsule elastometry does. Apart from these four methods there are other contact techniques such as probing capsules with AFM tips, micromanipulators, or optical tweezers (see Ref. [10] for a review). Pendant capsule elastometry is a non-contact technique and, in comparison with methods (iii) and (iv), it does not require fluid motion in the surrounding fluid. We focus here on elastic capsule shell materials. For viscoelastic materials there are other interfacial rheology methods available [25], such as double wall ring rheometry [31] or magnetic rod rheometry [32].

In shear-rheometry, a transducer (thin disk or ring) is placed in a circular vessel at a planar liquid-liquid or air-liquid interface; between transducer and container wall a membrane with the shell material is prepared, such that membrane deformations can be applied in circumferential direction. While oscillating at a certain frequency, the mechanical response is measured, which gives the interfacial storage modulus μ' and the loss modulus μ''. From μ' one determines the surface Young modulus $Y_{2D} = 2(1+\nu_{2D})\mu'$ provided that the Poisson ratio ν_{2D} is known.

In a Langmuir-Blodgett trough, a membrane made from the shell material is prepared in a rectangular vessel at a liquid-liquid or air-liquid interface. During compression of the membrane, the surface tension γ and area A are measured, from which the Gibbs modulus $E_{\text{Gibbs}} = d\gamma/d\ln A$ is determined. The Gibbs modulus E_{Gibbs} corresponds to the area compression modulus K_{2D} in the planar trough geometry; we will show that these two parameters differ substantially in the curved capsule geometry.

In a shear flow rheoscope, a closed capsule is placed in a liquid phase between two concentric hollow cylinders. By rotating the cylinders in opposite directions a shear flow is induced, which deforms the capsule. Comparing the shape profile with ellipses