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Mechanics of artificial microcapsules

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Abstract. In recent years, an increasing number of microcapsule systems have been realized and have found applications in various fields of research and technology. Amongst others, polyelectrolyte multilayer capsules (PMCs) offer a great variety of materials and superior control over the wall thicknesses. We present here a review on the different techniques that are available for characterizing the mechanical properties of PMCs. We compare results that were obtained using these techniques on the same system, namely PMCs made from polyallylamine and polystyrenesulfonate multilayers and discuss perspectives of the field.

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1. Introduction

Controlled encapsulation and release is an extremely important topic in many areas of daily life, e.g. in food sciences, life science and pharmacy, cosmetics, cleaning or printing and coating. In view of the many diverse applications there are also very different materials to be encapsulated,

and the requirements on capsules and walls vary drastically. Hence, it is not surprising that many different ways and systems have been tried and investigated and many of them are expected to find their application slot. To name a few extremes of capsule size, in the lower-nm range there are dendrimers [1] and guest–host or inclusion compounds, whereas in the high-nm range we have supramolecular aggregates similar to micelles and vesicles of low- and high-molecular-weight compounds [2]–[4] up to droplets and gel particles with diameters above 100 μm [5]. New developments have taken place in supramolecular and polymer chemistry [6], but as in other areas of technology the size range between 0.1 and 1 μm is especially difficult to achieve. New developments in colloidal science have been achieved recently and one of these will be the focus of this work. We will report on a concept which is attractive for physicists, because it does not require much chemical synthesis and is highly modular such that different properties can be tuned individually. For many applications most important properties are capsule wall permeability, adhesion and mechanics; here we will concentrate on the latter. For comparison of properties and techniques we also refer to other types of micro- and nanocapsules.

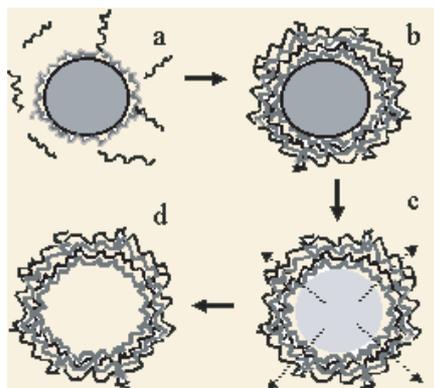
2. Systems

2.1. Polyelectrolyte multilayers

In the general concept, new techniques to prepare well-defined organic multilayers on planar support are adapted to coat colloidal particles. The method that has experienced most widespread attention in the past decade consists of adsorbing a polyelectrolyte (a polymer with many charged groups) on an oppositely charged substrate. Surprisingly, and not well understood, one achieves a stable charge reversal of the surface that can again be reversed by adsorbing the oppositely charged polymer [7, 8]. Thus one can obtain multilayers by cycling the adsorption process. Using x-ray and neutron reflection measurements it has been shown that surface roughnesses below 1 nm can be achieved, and also the roughness of inner interfaces was only 1–2 nm [9]–[12]. Thus, the thickness can be tuned in the nm range by a number of deposition cycles, chemical composition and preparation conditions [13]. The building blocks need not only be synthetic or natural polymers, but multiply charged organic [14] or inorganic particles [15, 16], proteins [17, 18], or multivalent ions [19] can also be used. Since cohesion mostly depends on many electrostatic interactions the system is stable against desorption, but since individual interactions are weak the structure depends on conditions during fabrication, partly also on later treatment. Thus, it was shown that film thickness depends on pH [20, 21], ionic strength [10, 22], humidity [23] and temperature [24], and also rearrangements can be achieved varying these parameters, the sensitivity depending on the actual composition. Of special relevance here is that generally the films are impermeable for large particles and polymers but permeable for entities with molecular weight <1 kDa. In the latter case, diffusion coefficients typical for polymeric glasses (10^{-14} – 10^{-16} $\text{cm}^2 \text{s}^{-1}$) were found, strongly depending on molecular size [25].

2.2. Multilayer capsules

Since films are constructed via adsorption the process can also be applied on curved surfaces, such as colloidal particles [26, 27] (Scheme 1). Indeed all available light scattering, neutron scattering and scanning force microscopy data point to the equivalence of the coating of planar or curved support. The particle is then dissolved or depolymerized, the conditions again depending



Scheme 1. Production of hollow polyelectrolyte multilayer capsules by coating of colloidal particles (a,b) and subsequent dissolution of the particles under conditions that do not destabilize the multilayers (c,d).

on the type of core [28]. Meanwhile, many types of inorganic, organic and even biological (cells) cores have shown to be feasible, but there is room for much improvement to get rid of all dissolution products and not to affect the wall by the process, either chemically or mechanically due to the osmotic pressure transiently established during core dissolution [25]. Thus, monodisperse capsules with diameters between 20 nm and 20 μm and with a uniform wall typically between 10 and 50 nm have been achieved. In the context of this review it is important that the mechanical properties can be varied in a broad range since materials can be selected from low-molecular-weight organic or inorganic compounds to stiff polymers and particles, and by sintering even porous inorganic composites can be obtained. Adhesion can be varied independent of the mechanics by adsorbing a ~ 1 nm thick outer layer with defined charge or specific binding units. Particle sizes around 1 μm are attractive for applications because the high volume/wall ratio (~ 100) enables a high payload. Still, our prime motivation to provide data on capsules with sizes above 1 μm results from the fact that, in this case, optical techniques are applicable that enable dynamic observations.

3. Mechanical properties

Although, as pointed out above, microcapsules can be built from a variety of materials, which is expected to lead to different mechanical properties, we limit ourselves here only to measurements of capsules made from multilayers of polyallylamine and polystyrenesulfonate. This is the best studied system in the field (see [29] for an overview). Since methods to characterize the mechanical properties of microcapsules are still evolving, the first task is to explore the limits and potential of different techniques. Therefore, we compare the results obtained using different methods on the same system. In general, we will distinguish between methods that use osmotic pressure effects to exert forces on the microcapsules and methods that rely on the micromanipulation of individual capsules.

3.1. Methods relying on osmotic pressure effects

Polyelectrolytes possess many dissociable groups, but for charge neutrality over distances of a screening length of typically below 10 nm there is a counter-ion cloud creating an osmotic

pressure π , which depends on the degree of dissociation and on the ionic milieu and can be measured by classical techniques. Hence, inclusion of polyelectrolytes in capsules causes an osmotic pressure tending to expand the volume; an outside polyelectrolyte tends to compress the capsule. Thus, an excess of polyelectrolyte inside or outside the capsule creates a uniform force, and the response yields information on mechanical properties. The effect of polyelectrolyte, in the solution, on the capsule shape was investigated by Gao and co-workers [30, 31].

Figure 1 presents a series of confocal fluorescence microscopy images of capsules, staining the wall by a dye, on increasing the outside polyelectrolyte (PE) concentration. One realizes that at low PE concentration all capsules are nicely spherical; however, at high PE concentration they are all deformed. By quantitatively measuring the fraction of deformed capsules as a function of PE concentration a critical osmotic pressure π_c can be derived where most capsules are nonspherical (figure 2(a)). By varying the wall thickness d the square dependence of π_c (figure 2(b)) can be obtained.

This dependence is expected for the Euler instability of a spherical shell with radius R and uniform wall thickness h , neglecting plastic deformations, according to

$$\pi_c = 4\mu \left(\frac{h}{R} \right)^2. \quad (1)$$

Hence, by knowing R we can derive the elastic modulus μ from the data in figure 2(b). In the specific case we obtain $\mu = 500$ MPa (corresponding to Young's modulus of $E = 1500$ MPa for a Poisson ratio of 0.5), a value which as expected was found to increase with molecular weight for the same pair of PE and also depends on the type of PE. The values of E are as high as typical for polymeric glasses similar to PMMA which is not what was initially expected. Actually one might expect that the experiment typically measures the weakest link allowing for an indentation which would yield a lower value of E and has no square dependence on h . Obviously, the wall is sufficiently homogeneous to enable application of this simple model. However, if one assumes a purely elastic response of the wall towards deformations, the capsules should fully collapse once the pressure is higher than the buckling threshold. This is not the case. Rather one finds a finite indentation that grows with the increase in osmotic pressure. This can be explained by partially plastic deformations of the material that limit the growth of the buckled zone.

3.1.1. Osmotic swelling of capsules. While in the first approach osmotic pressure was produced by increasing the concentration of PE outside the capsule, recently the swelling behaviour of capsules that were filled with PE was investigated. The capsules were filled with PSS by controlled precipitation using Y^{3+} ions [32], which could then be removed such that the PSS was redissolved and consequently exerted an osmotic pressure on the capsule membrane. The increase in radius depends on the concentration of the encapsulated polyelectrolyte. On the basis of this result, elasticity of the membrane material was estimated to be of the order of 100–300 MPa [33].

In general, the advantage of approaches that are based on the use of charged macromolecules to exert osmotic pressure on the microcapsules lies in the fact that with one experiment, the whole ensemble of capsules can be probed. In practice, the morphological changes that are induced by the osmotic pressure are monitored with confocal optical microscopy which adds some technical demands, but still hundreds of capsules can be probed in one experiment. The drawback of these methods is that forces cannot be changed *in situ* and high concentrations of macro-ions are necessary to induce pressures that are high enough to lead to deformations. At such high

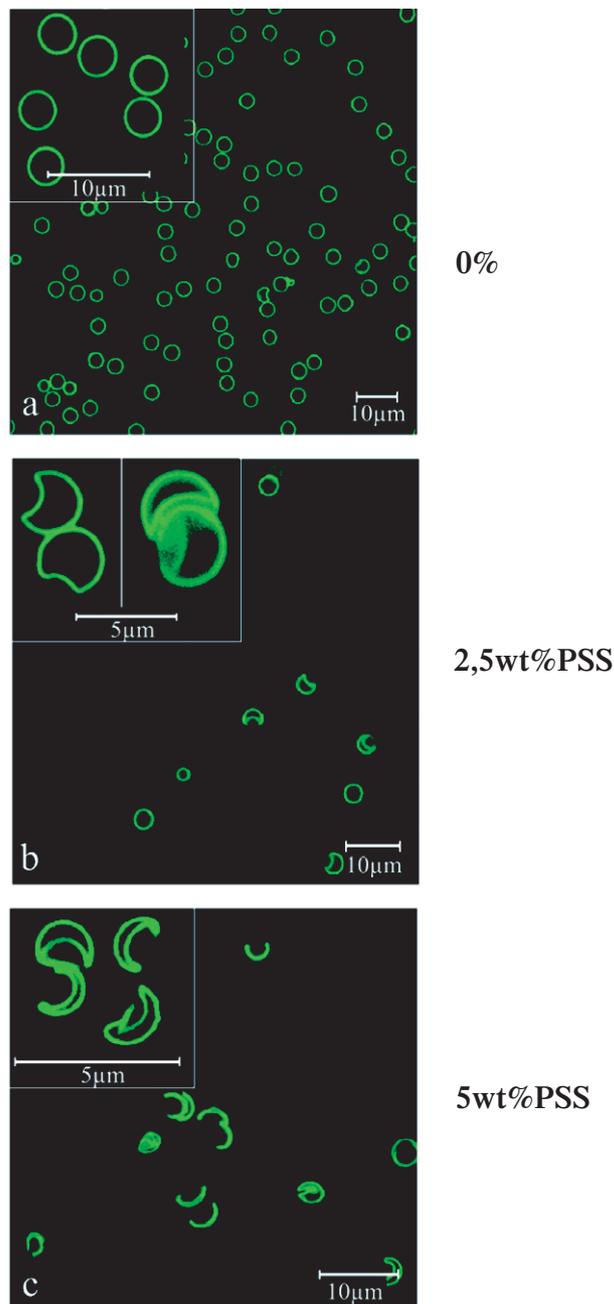


Figure 1. Confocal fluorescence microscopy images of polyelectrolyte capsules exposed to increasing concentrations of polyelectrolyte in the solution. In the polyelectrolyte-free solution (a), the capsules are spherical in shape, whereas the addition of polyelectrolyte leads to buckling of the capsule membrane and indentations appear (b,c).

concentrations, the osmolarity is no longer linear in the polyelectrolyte concentration and thus independent measurements of the osmotic pressure are necessary which have been carried out for the buckling studies [30, 31] and in the swelling studies [33]. In the swelling experiments, (quasi-) static situations are investigated, which have to be taken into account when comparing

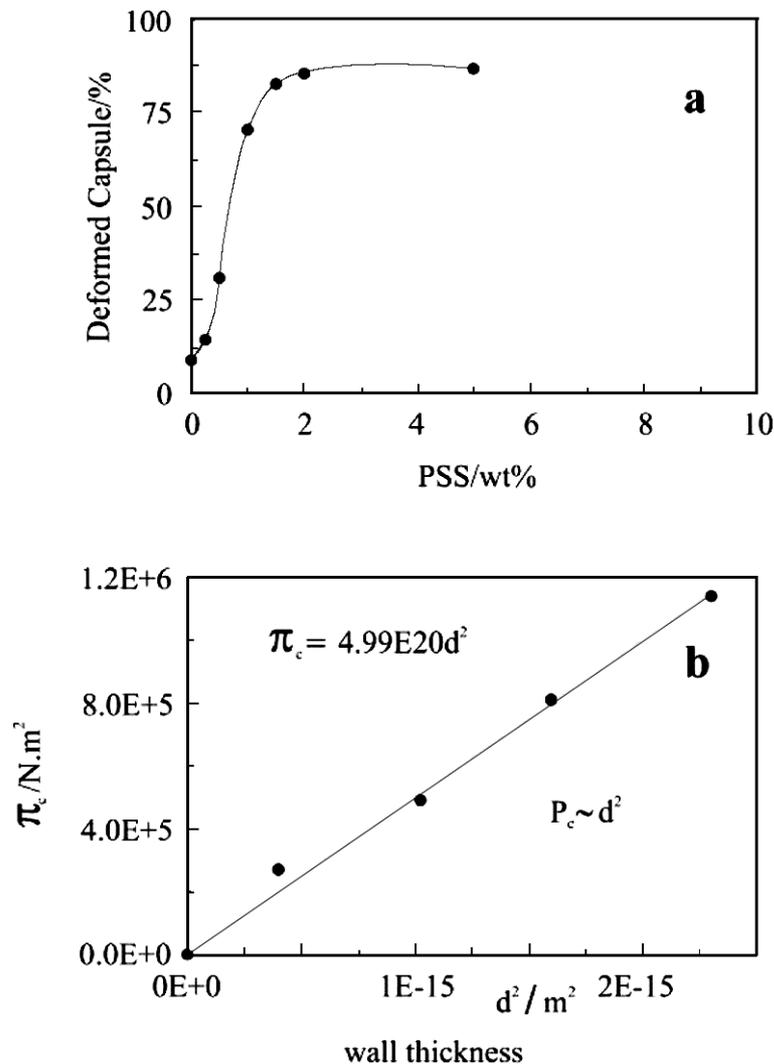


Figure 2. The critical osmotic pressure that leads to the capsule buckling instability can be determined from the concentration dependency of the percentage of buckled capsules in solution (a). Variation of the capsule wall thickness d for constant radius m shows the predicted quadratic dependency of the critical pressure on the wall thickness normalized on the radius (b).

values with other techniques: on the long time scale the material could molecularly rearrange in a viscoelastic fashion and thus lower elastic constants are to be expected.

3.2. Methods relying on micromanipulation of individual capsules

Methods that rely on micromanipulation of individual capsules are technically more demanding than the methods mentioned above and cannot offer good statistics since the whole ensemble is not probed in one experiment but only a limited number of capsules. However, they promise superior control over the applied forces, a greater range of forces and the possibility to change forces *in situ*. Thus, a lot of effort is put in this direction, using different approaches.

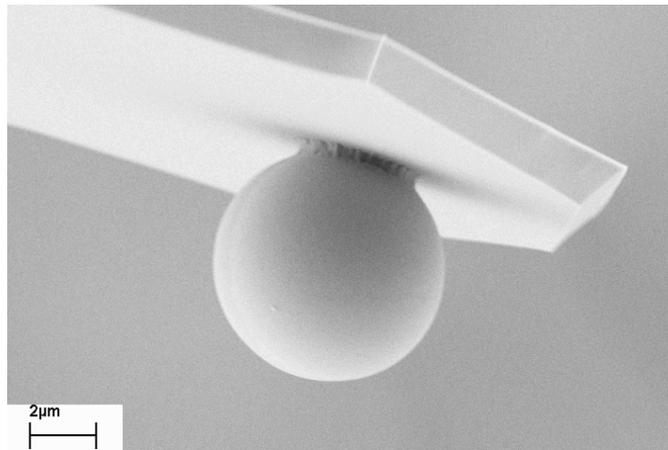


Figure 3. SEM image of a silica particle mounted on an AFM cantilever. The particles are glued to the cantilever using a micromanipulator and small amounts of glue (less than 10^{-15} l).

In the micropipette technique, which was originally introduced by Evans and Kwok [34, 35] and used for studying the mechanical properties of vesicles with great success [36], a micropipette of a few microns inner diameter is used to aspirate individual objects. Using hydrostatic pressure, small pressure differences can be applied across the membrane and the induced deformation can be monitored using optical microscopy. Bäumlér and co-workers [37] have used the micropipette technique for polyelectrolyte capsules. They observed that visible deformations only occurred for large pressure differences as compared with those typically found in vesicle systems (typically by a factor of 1000 higher). Also, the capsules' response was qualitatively different, since it was not possible to vary the area/volume ratio in a controlled and continuous way. Rather, the capsules showed no detectable deformation up to a critical pressure difference at which they collapsed and remained in collapsed form also after the pressure difference was released, showing a plastic deformation behaviour. The qualitative differences to the vesicle experiments can be understood by the fact that in the case of the capsule experiments reported above, no material creating an osmotic pressure was encapsulated. Thus, there is no mechanism that keeps the capsule volume constant. Consequently, the capsule collapses rather than being stretched. This problem could be overcome by encapsulating macromolecules as explained above. Still the plastic behaviour encountered complicates a quantitative interpretation.

The atomic force microscope (AFM) [38] can measure forces between 10^{-11} and 10^{-6} N and at the same time detect deformations smaller than 1 nm, which renders the technique an interesting candidate for microcapsule deformation studies. A general review on the use of AFM as a force spectroscopy instrument can be found in [39]. While in imaging AFM a sharp tip is interacting with the specimen, in the force spectroscopy the colloidal probe technique [40, 41] is widely used: a colloidal particle of several microns diameter is mounted on an AFM cantilever and is replacing the conventional AFM tip (figure 3 shows a scanning electron microscopy picture of a colloidal probe). The benefit of using a colloidal particle as a force probe lies in obtaining a well-defined geometry and at the same time increasing the sensitivity for small interactions by increasing the interaction area when compared with the sharp tip.

Attard and Gillies [42] first used the colloidal probe technique to study the deformation characteristics of viscoelastic particles resting on a flat substrate. The same approach was

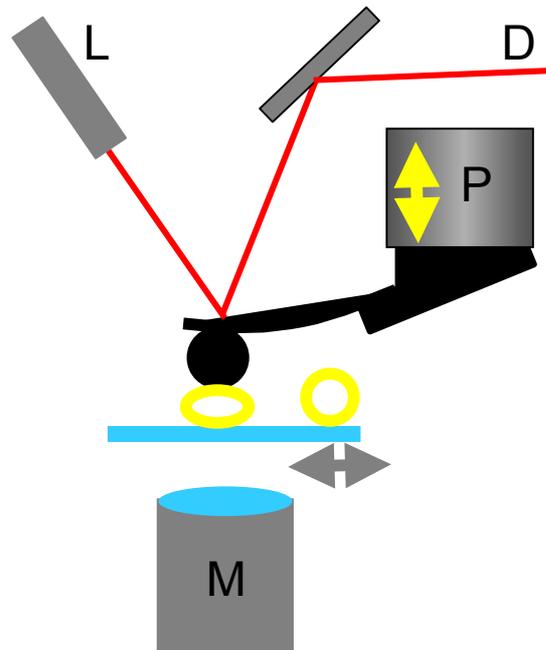


Figure 4. Schematic view of the colloidal probe AFM set-up used for studying PE-microcapsule mechanics: the piezo-crystal P is used to press the cantilever against the capsule resting on a flat substrate. The forces necessary to deform the capsule result in deflection of the cantilever that can be measured by the laserpointer method (the laser L is reflected from the cantilever and a position-sensitive detector D can thus detect small deflection changes).

independently used by Lulevic [43, 44] and Dubreuil [45] to probe the mechanics of polyelectrolyte microcapsules. Optical control was in both cases achieved by using a standalone AFM mounted on an inverted optical microscope as sketched in figure 4 (animation in movie 1 shows a schematic capsule measurement).

The first AFM studies focused on monitoring the force–deformation behaviour of microcapsules for large deformations from 20% of the capsule diameter up to 100% (total destruction of the capsules). It was found that forces in the low μN range had to be applied to induce such deformations. Capsules filled with polymer material showed about 10 times higher stiffness than non-filled capsules. Similar to earlier studies using the micropipette technique, a plastic deformation behaviour was found for high deformations. Whereas those experiments are valuable for application aspects of the microcapsules, where high deformations occur, a quantitative interpretation of the force–deformation data in terms of elastic constants of the wall material has so far proven to be complicated. Similar to the case of the micropipette measurements, the main problem lies in the fact that there is no physical mechanism that ensures a conservation of the capsule volume under a static load, unless the capsules are filled with osmotically active substances. However, in a dynamic experiment, the permeability of the capsule walls is expected to be of key importance for the effective stiffness of the capsules: if the compression is fast compared with the solvent permeation, the encapsulated volume is conserved and the main contribution to the resistance of the capsule against compression stems from the fact that to conserve the volume, the area of the membrane has to be increased (a sphere has the smallest area/volume ratio). Thus, the membrane has to be stretched and transient

tensions occur. If the transport of solvent across the wall is fast as compared with compression, these tensions are not created. The permeability of PE microcapsules for water molecules is not known; however, the permeability properties of the walls for larger molecular weight molecules have been studied intensively [25, 46, 47] and it is well known that the capsule walls are permeable for molecular weight $<10\,000$ (further treatment of the capsule can change their permeability drastically [24, 48]). The micropipette measurements as well show that large volume changes can occur on a time scale below the video resolution (20 ms) [37]. Thus, one expects not a full, but most probably a partial volume conservation depending on the rate of compression for dynamic measurements. The extent of volume conservation is as well expected to depend on the details of preparation since defects in the capsule walls can dominate the permeability. Consequently, attempts to derive elastic constants of the wall material from the large deformation behaviour assuming zero-membrane permeability have resulted in estimates of the Young modulus in the 1–10 MPa range [49], about a factor of a thousand to a hundred lower than found with other methods [30, 31, 33].

A possible way to overcome the problem of the unknown permeability/partial volume conservation that is present for large deformations is by measuring the capsules' small deformation behaviour: Irrespective of the permeability properties a hollow capsule reacts towards small deformations with a restoring force that is proportional to the deformation (the elastic response of the capsule wall material). The force F_{elast} scales [50] similar to

$$F_{\text{elast}} \propto \frac{4}{3} E h^2 \varepsilon. \quad (2)$$

If the membrane is impermeable, an additional restoring force arises since the membrane has to be stretched to keep the volume constraint when the spherical capsule is deformed. This volume constraint adds a term that scales as [50]

$$F_{\text{volume}} \propto \frac{16\pi}{3} E h R \varepsilon^3. \quad (3)$$

Here E denotes the materials' Young's modulus, h the wall thickness, R the capsule radius and ε the deformation normalized on the capsule diameter. Both formulae neglect prefactors of the order of 1 containing the materials' Poisson's ratio for the sake of simplicity. Owing to the different scaling in the deformation ε , the volume constraint loses its impact for sufficiently small deformations. Balancing the two terms shows that the relative deformation $\varepsilon_{\text{crossover}}$ of the crossover from the linear behaviour to the volume-constraint-dominated regime depends on both the wall thickness and the radius of the capsule:

$$\varepsilon_{\text{crossover}} \approx \sqrt{\frac{h}{4\pi R}}. \quad (4)$$

Figure 5 shows a direct comparison of the linear and volume-constraint contributions for a microcapsule of 50 nm wall thickness. More elaborate numerical calculations by Feng and Yang [51] and Taber [52] are in qualitative agreement with these simple scaling arguments.

To probe this regime, the sensitivity of the measurements has to be in the sub-nano-Newton range which was recently achieved by Dubreuil and Fery [45]. For capsules of 20 μm diameter and wall thicknesses of the order of 20–40 nm, deformations up to 200 nm (corresponding to $\varepsilon = 0.01$) were probed. A linear force–deformation relation was found (see figure 6 for a typical

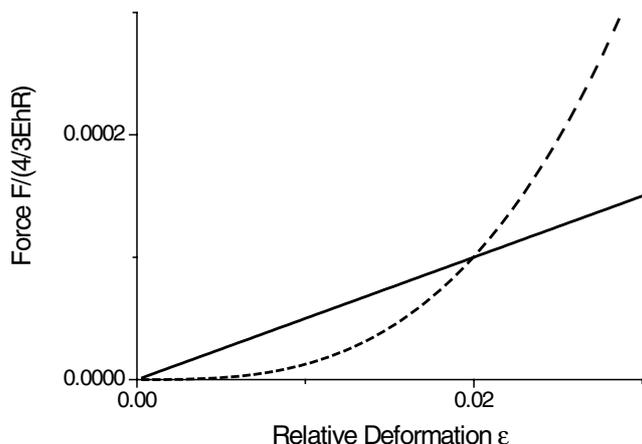


Figure 5. Comparison of the two main contributions with the capsule stiffness of a capsule of 50 nm wall thickness and 20 μm diameter (—: linear elastic membrane term; ---: volume-constraint term). Even for an impermeable membrane, the linear term dominates for small deformations. The crossover would be at 400 nm deformation. For finite permeability, the impact of the volume-constraint term further decreases and the crossover value shifts to higher ε .

force–deformation curve) and the quadratic scaling of the capsules ‘spring constant’ as predicted by the theory mentioned above was verified by using capsules of different wall thickness.

The elastic moduli derived from the measurements are of the order of 1.5–1.8 GPa and thus comparable with those found in the buckling experiments of Gao [30, 31] and a factor of 10 higher than those found in swelling experiments [33], which can be explained by the fact that different templates and different dissolution conditions were used in the latter experiments.

An interesting new development in this context is the combination of force spectroscopy with quantitative microinterferometry [45]. Using the microinterferometry technique, the shape of the capsules can be reconstructed from the interference pattern of monochromatic light reflected from the transparent substrate and the capsule walls. Previous work has shown that for simple geometries, a quantitative shape reconstruction with high lateral and vertical resolution can be obtained from the interference pattern. Thus, optical microscopy can be used not only for locating the capsules but also to derive information about the way in which they deform for a given force/loading rate. [Movie 2](#) shows the changes of the interference pattern during a loading–unloading cycle. [Figure 7](#) shows snapshots of the microinterferometry images during the deformation and the corresponding force–deformation curve: the discontinuities in the force deformation curve appear together with additional fringes in the central area. This is typical for a buckling instability of the membrane.

4. Conclusion and outlook

The mechanical properties of microcapsules are of obvious importance for practical applications, but they are also an intriguing object to study for physical reasons. Shells can be prepared with a high definition of layer thickness with layers of components drastically different in mechanical properties. It is this nanocomposite character which also lends abalone, muscle or bones their

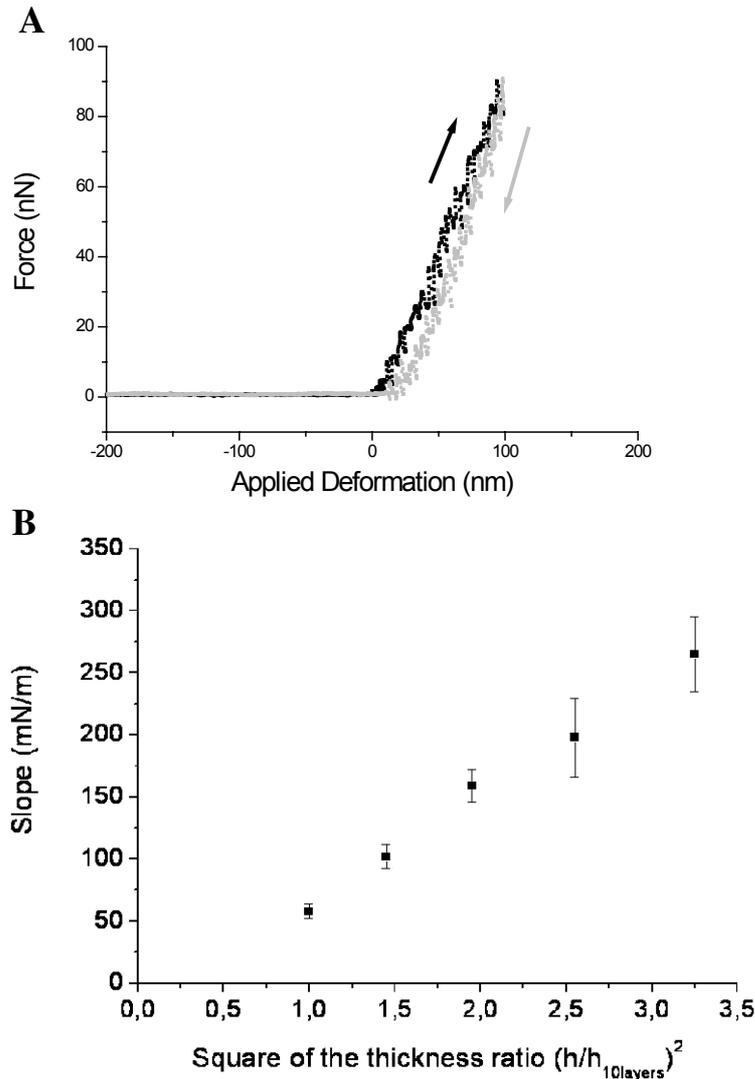


Figure 6. (A) A typical force versus deformation characteristic of a hollow capsule for small deformations ($\epsilon < 0.01$); the deformation is proportional to the applied force. (B) The slope of the force deformation curve is plotted as a function of the squared wall thickness. A quadratic scaling which rules out volume contributions as discussed above is seen.

unique mechanical strength. It has become apparent that rather elegant and complementary techniques have become available to derive quantitative data on individual shells. For future work it appears most promising to study the relation between modulus, adhesion and local curvature of shells as well as shape transitions. For the systems we have presented one expects that mechanics and adhesion can independently be varied which appears most promising also for applications [53]. Also for polyelectrolyte multilayer capsules, we show that the laws of continuum mechanics hold down to dimensions of the order of 10 nm. Future trends in this area concern the limits of continuum mechanics, dynamic forces and the importance of structural transitions within individual layers.

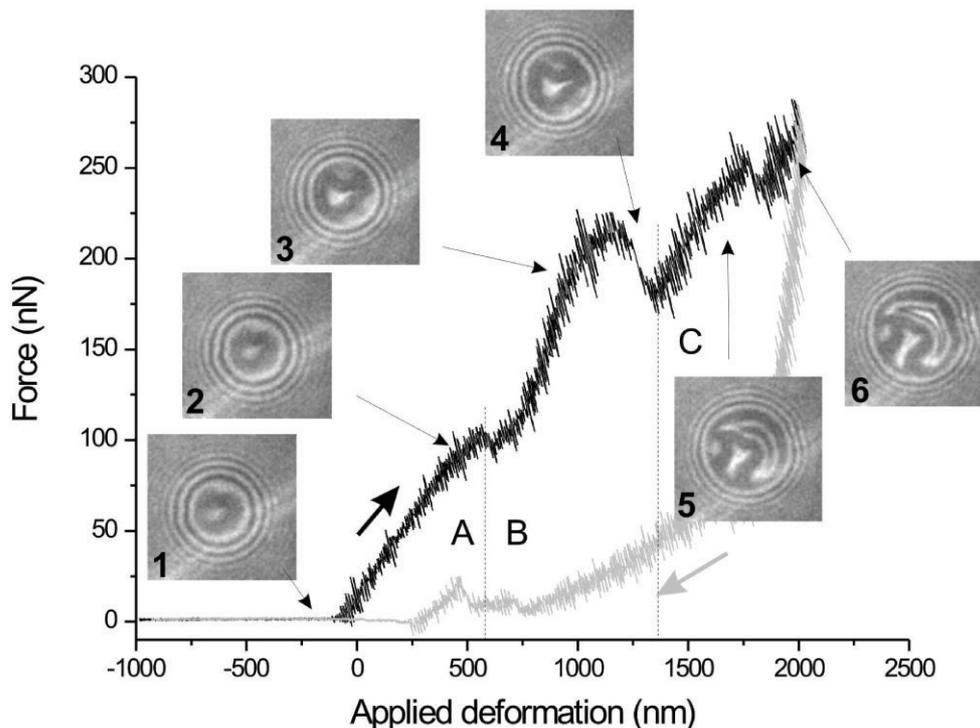


Figure 7. Snapshots of the microinterferometry images during the deformation as insets in the force–deformation curve. Labels A, B, C refer to deformation regimes: (A) no change in the contact area is noticed (pictures 1 and 2 are identical), in (B) an increase in the adhesion area is observed (increase in the central dark zone in pictures 2–4) and (C) a buckling of the capsule in the adhesion area took place (fringes inside the central area in pictures 5 and 6).

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