Available online at www.sciencedirect.com

ScienceDirect

Procedia IUTAM 16 (2015) 12 – 21

Procedia IUTAM

www.elsevier.com/locate/procedia

IUTAM Symposium on Dynamics of Capsules, Vesicles and Cells in Flow

Deformation, orientation and bursting of microcapsules in simple shear flow: Wrinkling processes, tumbling and swinging motions

Anja Unverfehrt[a*], Heinz Rehage[a]

[a]*TU Dortmund, Chair of Physical Chemistry II, 44227 Dortmund, Germany*

Abstract

In a series of experiments we systematically investigated the orientation and deformation behavior of non-spherical capsules in simple shear flow. We observed a continuous capsule rotation at low shear rates, denoted as *tumbling mode*. A *swinging mode* at elevated shear rates was characterized by oscillations of the inclination angle around positive values, superimposed by a *tank-treading* motion of the capsule membrane. The transition between these different modes occurred via an *intermittent regime*. It turned out that the capsule deformation greatly influenced the orientation dynamics. In several experiments, we also observed shear-induced membrane wrinkling processes.

Peer-review under the responsibility of the organizing committee of DYNACAPS 2014 (Dynamics of Capsules, Vesicles and Cells in Flow).

Keywords: Non-spherical capsules, shear-induced deformation, membrane tank-treading, tumbling, swinging

1. Introduction

Microcapsules are widely spread in industrial and daily life. The field of application ranges from food technology and cosmetics to pharmaceutical and medical products. According to technical requirements a variety of capsules with well-defined wall materials needs to be designed. Tailor-made hollow particles with controlled release properties and bursting processes are of great interest because they serve as transport carriers for different types of ingredients. On grounds of these special features, the knowledge of the mechanical properties of the membrane is indispensable. Besides technical or medical applications microcapsules can also be used as model systems for

* Corresponding author. Tel.: 0049-231-755-3935; fax: 0049-231-755-5367.
E-mail address: anja.unverfehrt@tu-dortmund.de

Peer-review under the responsibility of the organizing committee of DYNACAPS 2014 (Dynamics of Capsules, Vesicles and Cells in Flow).
doi:10.1016/j.piutam.2015.03.003

biological cells, e.g. erythrocytes. It is well-known that red blood cells (RBCs) have the ability to resist shear forces in blood flow and, due to their high deformability, these particles can slide through narrow capillaries. After passing these obstacles, they relax and reach their initially shape[1,2]. RBCs seem to have a special shape memory[2]. These unusual properties are based on the structure of the membrane. It consists of a lipid bilayer underlined by a spectrin-network giving the RBC its viscoelasticity. In order to understand the complicated rheological properties of biological cells, we investigated artificial microcapsules in simple shear flow. These particles simply consisted of fluid droplets, which were surrounded by a thin, flexible polysiloxane membrane. Due to different polymerization techniques, we could adjust the viscoelastic properties of the surrounding polymer layers. This variation allowed studying basic flow principles and orientation mechanisms.

An adequate model to describe the deformation and orientation behaviour of initially spherical microcapsules in simple shear flow was first developed by Barthès-Biesel[3]. In this theoretical approach, the liquid core of the capsule is surrounded by a thin, impermeable membrane characterized by the surface Young´s modulus E_s[4]. Both the inner and the outer fluid are incompressible Newtonian liquids with viscosities η_i and η_o. Under shear forces the capsule is deformed to an ellipsoid with the axis lengths L and B (Fig.1).

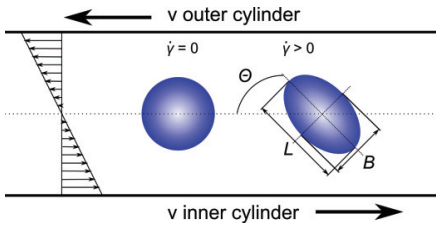

Fig. 1. Deformation of an initially spherical capsule in simple shear flow.

As a result of the deformed state, the particle is orientated towards the streamlines at an inclination angle Θ. The deformation of the capsule is given by the Taylor-Parameter D (eq. 1).

$$D = \frac{L - B}{L + B} \tag{1}$$

For purely elastic membranes obeying Mooney Rivlin´s law, the model proposes a constant inclination angle of $\Theta = 45°$ (when $C_a << 1$) and a linearity between D and the Capillary number C_a (eq. 2). Here η_o denotes the viscosity of the outer solvent, $\dot{\gamma}$ describes the shear rate and r is the radius of the capsule in the quiescent state.

$$C_a = \frac{\eta_o \cdot r \cdot \dot{\gamma}}{E_s} \tag{2}$$

Many parameters such as the initial shape[5,6], the viscosity ratio λ of the inner and the outer phase[7-9], the bending stiffness[10-12], the membrane pre-stress[13], the membrane constitutive laws[14,15], and wrinkling instabilities[15-18] influence the deformation, orientation and bursting process of a capsule. For non-spherical capsules the situation even becomes more complicated because they show oscillation phenomena. A *tumbling mode* (TU) was predicted, characterized by a periodic variation of the inclination angle Θ between +90° to -90° [8,17]. During this motion the capsule rotated continuously like a solid particle around its principal axis. The *swinging mode* (SW) describes the oscillation of the inclination angle around positive values[8,17,19]. This special motion is accompanied by the membrane rotation around the fluid core (*tank-treading* (TT))[8,17,19,20,21]. The latter was also proposed for spherical capsules in steady state shear flow[3,5,15,20]. It was predicted, that the transition between these two modes occurs via

altering the shear rate $\dot{\gamma}$ [5,17,19,22], the viscosity ratio λ [7,8,21] or the membrane viscosity[23]. The model of Skotheim and Secomb[24] expects a narrow *intermittent regime* (IR) where alternating swinging and tumbling capsule motions occur. The existence of such a transition state was experimentally proved by recent results of Abkarian *et al.*[19] and Koleva *et al.*[17].

In a series of additional experiments we investigated anisometric microcapsules in simple shear flow by means of an optical flow cell (rheoscope). These measurements were performed in order to get more insight into the complicated rheological properties of non-spherical, ellipsoidal capsules.

2. Experimental

The microcapsules were synthesized by interfacial polymerization of emulsion droplets. The disperse oil phase contained monomers of *n*-octadecyltrichlorsilane (OTS), which immediately hydrolyzed to the corresponding alcohols in contact with water. The hydrophilic OTS molecules adsorbed at the oil-water interface, reacted with water to the corresponding alcohols (silanols) and subsequently polymerized to polysiloxanes due to the condensation reaction between the alcohol groups[25]. The interfacial polymerization and gelation reactions were carried out under slightly alkaline conditions.

A simple structured microfluidic-device ensured a nearly monodisperse distribution of droplet sizes[17]. In this device the disperse oil phase was injected vertically to the flow direction of a continuous aqueous phase. The velocities of the liquids were controlled by automatic syringes. The generated droplets were collected in a beaker and stored in this container until the membrane was formed. Coalescence, sedimentation or creaming processes were prevented by density adjustment and the high viscosity (261 mPas) of the continuous phase. The aqueous solution consisted of 90 wt% glycerol and 0.5 wt% NaOH (ρ = 1.241 g/cm³). In the disperse phase a mixture of *p*-xylene, *1.2.4*-trichlorobenzene (ρ = 1.243 g/cm³) and 0.4 mM of OTS were dissolved. Using the microfluidic-device we succeeded to produce capsules with diameters of about 300 µm.

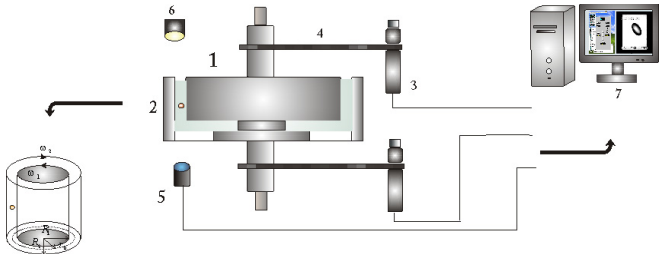

Fig. 2. Schematic drawing of the rheoscope: 1-inner cylinder (height 10 mm), 2-outer cylinder, 3-motor drive unit, 4-belts, 5-microscope objective, 6-light source, 7- software processor[17].

The optical flow cell (rheoscope) consisted of a coaxial cylinder system which was inserted into an inverse microscope. Due to the different radii of 42.4 and 41.0 mm a gap of 1.4 mm was formed[17]. This cavity was filled with a high viscous solvent to achieve a small Reynolds number. All experiments were carried out with anhydrous glycerol to prevent the capsules from further polymerizations. We applied a laminar shear field and a stagnation zone by rotating the cylinders in opposite directions. The capsules produced in the microfluidic-device were placed via a syringe into the center of the annular gap. Due to a glass bottom in the outer cylinder, the capsules were observed during flow. Measurements were performed with increasing, decreasing or constant shear rates and analyzed by means of a high speed video camera (Kodak SR Corder Motion Analyzer). A video file with 25 frames/s and a log file with the value of the shear rate were recorded simultaneously. The deformation and orientation of the capsules were calculated from the contour and alignment using the NI VDM software. A detailed description of the rheoscope is given in reference 26.

The solvents *n*-octadecyltrichlorosilane (ABCR), *p*-xylene (99+%, Sigma-Aldrich) and *1.2.4*-trichlorobenzene (99+%, Sigma-Aldrich) were stored under argon. As OTS is extremely reactive towards small amounts of water we used anhydrous solvents. Their water content (about 0.0025 wt% H_20) was determined by Karl-Fischer-Titration. Anhydrous glycerol was purchased from Merck.

3. Results and discussion

The formation and the membrane properties of ultra-thin polysiloxane networks were investigated in an interfacial shear rheometer. To estimate the polymerization time of capsules we determined the kinetics of surface gelation in time-sweep-tests. The gel point describing the sol-gel transition was reached after about 20 min (results not shown). The plateau value of the two-dimensional storage modulus μ' indicates the end of polymerization after about one hour (results not shown). The dynamic properties of the ultra-thin polysiloxane networks were explored in frequency-sweep-test. The storage modulus turned out to be independent of the frequency which is characteristic of a chemical cross-linked network[27]. In strain-sweep-tests we discovered a small linear-viscoelastic regime of less than 1 % (results not shown). The mean value of the surface shear modulus of the capsule membrane was determined from frequency-sweep-experiments. Using the theory of Barthès-Biesel (Eqn. 2) we could also measure the surface Young modulus of polysiloxane capsules from measurements performed in the rheoscope analyzing the slope between D and $\dot{\gamma}^4$. It turned out, that all these different measurements were in fairly good agreement, just confirming the model of Barthès-Biesel[4]. As results, we obtained a surface shear modulus $\mu_s = 0.4$ N/m, a surface Young modulus $E_s = 1.7$ N/m and a Poisson number $\nu_s = 0.8$ for a concentration of $c_{OTS} = 0.4$ mM[28].

In this present study we shall now focus on the more complicated case of non-spherical capsules which always had a constant viscosity ratio of $\lambda = 0.001$. It turned out that the deformation and orientation behaviour of these anisometric particles depended very much on the shear rate. In the regime of low shear rates we observed a *tumbling mode* (TU) (fig. 3). Under these conditions, the inclination angle varied periodically between +90° to -90° (fig. 4). This movement corresponds to a half rotation period. In other words, the capsule performed a complete rotation movement when the angle varied twice between +90° to -90°. According to this motion, we may state, that the capsule simply behaved like a rigid particle. Close inspection, however, revealed that due to the presence of a flexible membrane the capsules also exhibited accompanying shape oscillations (fig. 4, blue curve). The detailed analysis showed that the oscillation of the inclination angle was asymmetric. Following Bagchi and Kalluri[8], we denoted the time the capsule did spend in the extensional quadrant of flow as τ_2 ($0° < \Theta < +90°$). Similar to this definition, τ_1 represented the time, the capsule did stay in the compressional quadrant of flow ($-90° < \Theta < 0°$). Our measurements showed that $\tau_2 > \tau_1$. Thus the capsules rotated faster, when directed with their main axis opposite to the stream lines (fig. 3c). This means that the particles did spend more time in the extensional quadrant of flow. These results agree, at least qualitatively, with numerical simulations of Bagchi and Kalluri, who focused on the coupling between shape deformation and orientation dynamics. The theoretical analysis was performed for non-spherical particles for a broad range of viscosity contrast, axis ratios and shear rates (respectively C_a)[8]. Our experimental results with very low viscosity ratios λ and Capillary numbers ($C_a << 0.1$) were, nevertheless, not directly calculated. It is, therefore, not possible to compare the experimental results and the theoretical predictions quantitatively. The striking characteristics of the modes, however, are in good agreement. The Keller and Skalak theory, for instance, which neglects the deformability of the particles, predicts a fluid-like tumbling mode[7]. With decreasing viscosity contrast λ an asymmetric tumbling motion occurs, and the capsules are finally oriented at an inclination angle which depends on the shear rate and the capsule axio-ratio[7]. An interesting question, in this context, is related to the movement of the surrounding capsule membrane. As the particles, we synthesized, did not show any defect in the vicinity of their flexible interfaces, we could not visualize the membrane rotation. This is

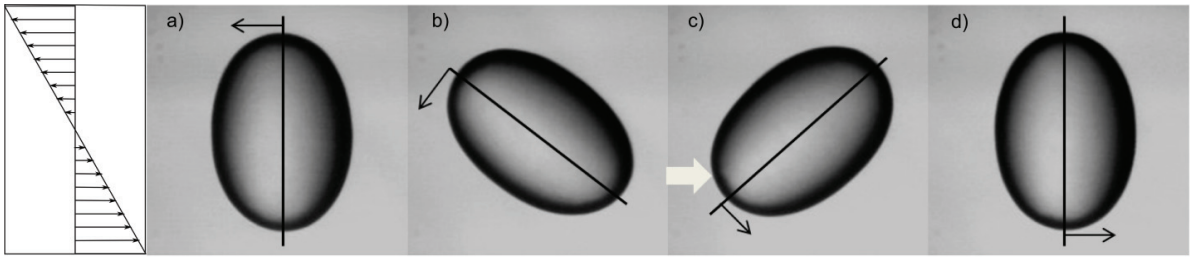

Fig. 3. Tumbling capsule from +90° to -90° with an axis ratio $B/L = 0.9$; $\dot{\gamma} = 2\ s^{-1}$

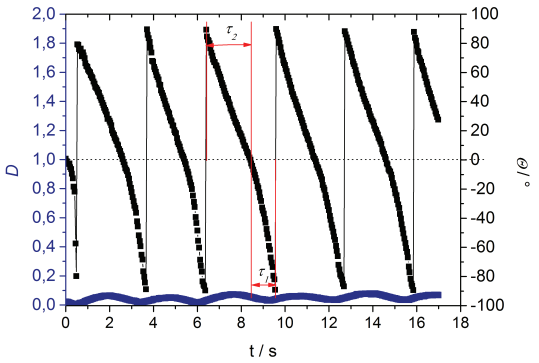

Fig. 4. Tumbling mode with asymmetric oscillations; $B/L = 0.94$; $C_a = 0.0004$.

only possible if some markers as nanoparticles or glass spheres are firmly attached to the cross-linked membranes. At the present state it remains, therefore, unclear whether the membrane oscillates, drifts or really exhibits rigid-like properties.

The angular tumbling frequency ω_{TU} did depend on the shear rate $\dot{\gamma}$. We calculated this value according to the simple equation $\omega_{TU} = 2\pi/T$, in which the period T described the time the capsule needed for a complete revolution. We determined the ratio $\omega_{TU}/\dot{\gamma}$ to be 0.46. This roughly corresponds to the simple correlation:

$$\dot{\gamma} \approx 2 \cdot \omega_{TU} \tag{3}$$

Equation (3) is analogous to the correlation between the shear rate and the *tank-treading* frequency of spherical capsules which are surrounded by purely elastic membranes[29]. Similar to the results obtained for lipid vesicles[30], deviations may arise from energy dissipation by the internal fluid. The work produced by the streaming external fluid is therefore not totally transformed in kinetic energy for the capsule rotation. The discrepancy is maybe also caused by the influence of the membrane viscosity. From frequency-sweep measurements, which were performed at the plane interface, we could determine the surface storage modulus μ' and the surface loss modulus μ''. The magnitude of the complex membrane viscosity can be calculated by means of the simple formula,

$$\left|\eta^*\right| = \frac{\sqrt{(\mu')^2 + (\mu'')^2}}{\omega} \tag{4}$$

Typical results of the magnitude of the complex membrane viscosity are represented in Fig. 5a. It is evident that the complex viscous resistance of the membrane varies over many orders of magnitude, and that the sample exhibits the typical shear-thinning behaviour of viscoelastic polymers. The absence of a plateau in the regime of very small angular frequencies points to the existence of chemically cross-linked network structures. For concentrated polymer solutions and polymer melts, it was often observed that the magnitude of the complex viscosity coincides very well with the steady-state shear viscosity, if equal values of the shear rate and angular frequency were compared. This phenomenon is quantitatively described by the famous Cox-Merz rule[27]. As a consequence of this analogy, we can interpret the magnitude of the complex viscosity as the viscous resistance of the membrane. The striking non-linear behaviour of the membrane viscosity is not yet included into theoretical models and may cause slight deviations of the angular tumbling frequency of the microcapsules from the value of 0.5.

At high shear rates we observed a *swinging mode* (SW) for ellipsoidal capsules. The capsule was now orientated in the extensional quadrant of flow and oscillated around positive angles (fig. 5b). As well as in the tumbling regime the oscillations were asymmetric. In this case τ_1 denoted the time the capsule turned from Θ_{min} to Θ_{max}, and τ_2 the

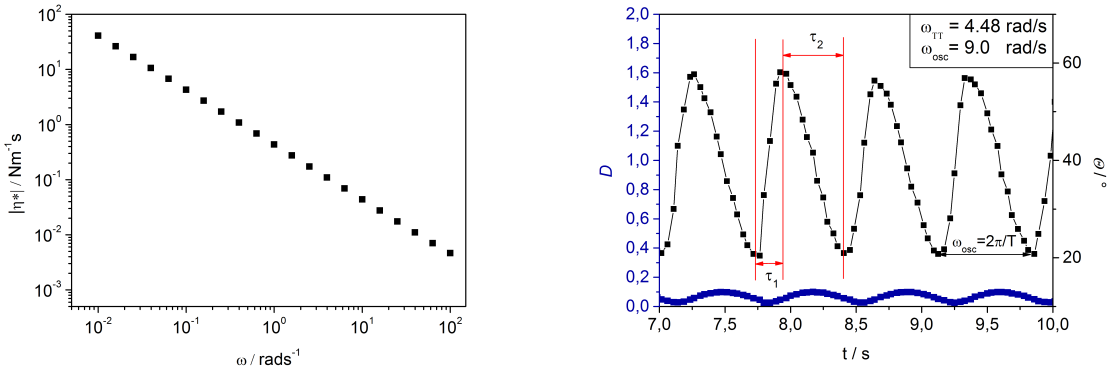

Fig. 5. (a) Magnitude of the complex viscosity as a function of the angular frequency; (b) Swinging mode; $B/L = 0.94$, $C_a = 0.002$.

period the capsules oscillated back from Θ_{max} to Θ_{min}. Again τ_2 was significantly larger than τ_1. This means that the capsule swung faster in the opposite direction to the rotational motion of flow. Bagchi and Kalluri explained this movement by the shape deformation[8]. The compression of the capsule occurred over a longer time than the elongation. The capsule was exposed to compressive stress, even when it was directed with its main axis in the extensional quadrant of flow[8]. Fig. 6 represents different capsule shapes during the swinging motion. Fig. 6b shows the particle in an elongated state while the capsule in fig. 6e is evidently more compressed.

The *swinging mode* was superimposed by a membrane rotation, the *tank-treading* motion. This special movement can be observed when small particles stick on the membrane (fig. 6). The angular tank-treading frequency ω_{TT} was calculated analogously to ω_{TU}. In this case the period T corresponded to the time a membrane element performed a complete rotation around the core back to its initial position. It turned out that the tank-treading frequency is approximately half of the oscillation frequency,

$$\omega_{TT} = \frac{\omega_{osc}}{2} \tag{5}$$

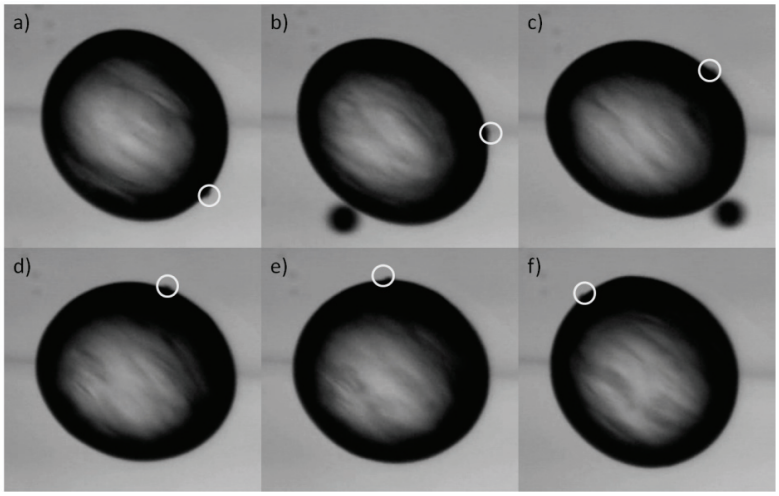

Fig. 6. Swinging mode: the white ring illustrates the rotation of a marked membrane element during a tank-treading-motion.

This observation confirms the experimental results for RBCs[19] and Polyamide microcapsules[16] and agrees well with the theory of Skotheim and Secomb[24]. These authors extended Keller and Skalak's theory by including a membrane elastic energy and hence the shape memory effect. In contrast to spherical capsules membrane elements of anisometric particles are not equivalent and unstrained at rest. During the tank-treading motion, a membrane element, which formed the rim for example, rotated around the capsule core changing its position. It was locally strained and stored thereby energy. Reaching the other side of the rim and its initial position, the energy decayed to its minimum value. Thus two minima of the elastic energy were passed during one tank-treading cycle for which reason the particle (non-spherical capsule or RBCs) oscillated twice about their mean inclination angle[19,24].

The swinging amplitude and the average inclination angle decreased with increasing shear rate (results not shown) as it was already found in previous experiments[16,17,19] and numerical simulations[5,8,22]. This phenomenon can be explained by more elongated shapes at higher shear rates[8].

The transition from tumbling to swinging occurred via an *intermittent regime* (IR). The inclination angle did not reach +90° or -90° anymore, and we also did not detect a pure swinging mode at positive values. We observed, instead, variations from +80° to -80° or 85° to -40°. It is evident, that this mode differed from that predicted by Skotheim and Secomb[24]. These authors suggested a narrow regime of alternating tumbling and swinging motions. Similar modes were found for non-spherical particles with intermediate viscosity contrast[8,23]. It was denoted as *vacillating-breathing* (VB).

In the *intermittent-regime*, the inclination angle attained positive and negative values without reaching ± 90°. The explanation for the appearance of such motions, however, is similar to that of the *VB-mode*. Bagchi and Kalluri. took the strong coupling between shape deformations and inclination angles into account[8]. As shown in fig. 7 we observed large shape deformations. The capsule was continuously compressed ($\Theta < 0$) and elongated ($\Theta > 0$). It is worth mentioning that compression and elongation were more significant in the *IR-region* than in the *TU-regime* due to the enhanced shear forces. It is evident that D became nearly zero in this region (fig. 7). The capsule reached instantaneously a quasi spherical shape. The reduced hydrodynamic torque prevented the capsule from making a full tumble[8]. With increasing shear rate, shear forces were sufficient to overcome the maximum elastic energy during a tank-treading cycle[24]. As a consequence, the transition to the swinging mode took place.

As shown in fig. 6 buckling sometimes occurred during shear flow. This phenomenon arose only for a selected amount of capsules. The wrinkles appeared at low shear rates due to principal negative tensions[13,15,31]. The existence of a finite bending stiffness generally prevented buckling as long as shear forces were small. In recent experiments

we determined the membrane thickness and bending stiffness in pendant-drop experiments[32]. These measurements were based on analyzing the contour and wavelengths of the wrinkled capsules. The membrane thickness was estimated to be 0.8 µm, whereas the bending stiffness was $E_B \approx 2.5 \cdot 10^{-14}$ Nm. It should be noted, however, that in these experiments the polymerization occurred under slightly different conditions as pure solvents, water and *p*-xylene, were used. That might be the reason why the calculated bending modulus was considerably larger than the one estimated by Finken and Seifert ($E_B = 1 \cdot 10^{-17}$ Nm)[31]. These authors examined the distances between the folded

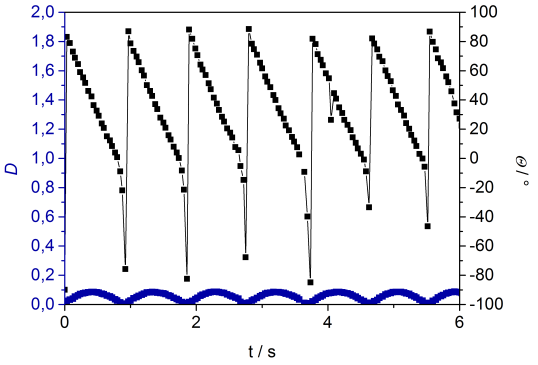

Fig. 7. Intermittent regime; $B/L = 0.94$, $C_a = 0.0015$.

regions of polysiloxane capsules in shear flow[16]. The large discrepancy between these two results can be mainly explained by different membrane thicknesses, because the bending resistance depends very much on this parameter. In this context it is interesting to note that the calculated membrane thickness, which was obtained by pendant-drop experiments, was in good agreement with cryo-TEM measurements[26]. Hence we can conclude that the resulting bending stiffness of polysiloxane membranes was obviously not sufficient to prevent buckling. Lac and Barthès-Biesel proposed that osmotic pressures and the resulting pre-stress led to positive tensions and that this effect avoids crumbling[13]. As the solubility of water molecules in the oil phase was very small and no swelling or shrinking processes could be observed, osmotic pressures can be neglected in this case[17].

In recent numerical simulations, Yazdani and Bagchi[23] took the membrane viscosity into account. These authors suggested that elevated values of membrane viscosities lead to buckling in the absence of bending rigidity. However, this influence was marginal at low C_a which we investigated in this publication. In addition, wrinkles disappeared with increasing viscosity ratio λ for a given membrane viscosity[23]. Very low values of λ, which we investigated, should consequently lead to buckling processes. Foessel *et al*[9]., on the other hand, predicted that viscous capsules easily tend to buckle beyond a critical value of λ. The present study, however, showed that wrinkles appeared already at very low viscosity ratios. In addition, investigations of Koleva[26] revealed that polysiloxane capsules with $\lambda = 1.34$ exhibit wrinkles even in the quiescent state which would support the model of Foessel *et al.*. On grounds of this limited information, further studies are necessary to understand the influence of the bending resistance and the membrane viscosity on shear-induced folding processes.

4. Conclusion

In a series of different experiments, we studied the rheological properties of non-spherical capsules in simple shear flow. It turned out that the orientation and the deformation of these anisometric particles were strongly linked and dependent of the shear rate. We observed three different deformation and orientation types with increasing shear rate: A tumbling mode, characterized by a continuous capsule rotation, an intermittent regime, in which the capsule failed to perform a full tumble and a swinging mode. During the swinging mode the inclination angle varied

periodically around a mean orientation angle. This mode was accompanied by the tank-treading motion of the surrounding membrane. Our measurements confirmed a well-known correlation between the tank-treading motion and the oscillation frequency. In agreement with RBCs the capsule oscillation frequency was approximately twice as large as the tank-treading angular frequency. The elastic energy of the membrane and the shape memory effect might be responsible for this observed phenomenon. RBCs and polysiloxane capsules share a crucial property, the surface shear elasticity. The existence of a lipid bilayer of cells and vesicles, however, also provokes major differences. It is well-known that the incompressibility of this membrane leads to conservation of the membrane surface area. This geometrical constraint finally generates the striking non-linear membrane response of lipid bilayers compared to the deformation of an elastic network. For RBCs the underlying spectrin network is also responsible for shape memory effect[2]. Besides these differences, there is still an undergoing debate if the resting shape of RBCs is stress-free[33]. Similar to this discussion, we have several arguments why the membrane of our non-spherical capsules might also be pre-stressed. As the capsules were produced during flow in the microfluidic device, the formed membrane must, even during synthesis, prevent further capsule elongation, and this is only possible if the membrane is under stress. If we remove the shear field after the capsule formation, the particles relax back to a quiescent, non-spherical shape. From previously performed spinning-capsule experiments, we have strong evidence that the membrane of non-spherical capsules is pre-stressed, even in the quiescent state[34]. It is conceivable that similar phenomena can also occur for anisometric capsules which are formed in shear flow. As a consequence, we cannot decide at the present state whether the capsules, after synthesis, relax back to an equilibrium state where the membrane is still under tension or not.

It is certainly an interesting approach to compare our experimental results with the general phase diagram, which was recently proposed in Ref [21]. As the synthesis of the capsules is complicated and the density differences have to be properly adjusted after each changing of the solvents, it is extensive work to systematically change the viscosity contrast λ. The variation of the solvents and the addition of supplementary compounds generally have influence on the kinetics and the mechanisms of the membrane gelation, and the structure and properties of the cross-linked networks such as thickness, pore-size distribution and elasticity are also changed. From an experimental point of view it is therefore not so simple to vary λ systematically.

The phase diagram of non-spherical capsules in Ref [21] was calculated for an axial ratio of 0.9 and the elastic parameters were given by the Poisson number (ν = 0.333) and the dimensionless bending rigidity ($\widetilde{\kappa}$ =0.01). Our capsules, however, showed different axis-ratios and elastic properties with typical values of ν = 0.8 and $E_B \approx 2.5 \cdot 10^{-14}$ Nm[32]. On the grounds of these discrepancies, it is yet not possible to compare our experimental results with the model of Kessler *et al*. It is, however, evident that we observe all phases and phenomena which were recently predicted by theory. As a result of different experiments, we know all important properties of our capsules, so that we do not have free fitting parameters. Hence these anisometric particles might be used in order to get more detailed insight into the shear induced orientation and deformation of non-spherical microcapsules.

In additional measurements we also plan to investigate polyacrylamide membranes which are more flexible and which have smaller elastic moduli. As artificial capsules can be synthesized with different sizes and shapes and their mechanical properties are tunable, these particles might serve as useful model systems.

Acknowledgements

We would like to thank the “Deutsche Forschungsgemeinschaft” (DFG, RE 681/24-1) for intensive support of this study.

References

1. Sackmann E, Mikromechanik der Zelle. *Physik Journal* 2004;**3**:35-42.
2. Fischer TM, Shape Memory of Human Red Blood Cells. *Biophys J* 2004;**86**:3304-3313.
3. Barthès-Biesel D, Motion of a spherical microcapsule freely suspended in a linear shear flow. *J Fluid Mech* 1980;**100**:831-851.
4. Barthès-Biesel D, Mechanics of encapsulated droplets. *Progr Colloid Polym Sci* 1998;**111**:58-64.

5. Sui Y, Low HT, Chew YT, Roy P, Tank-treading, swinging and tumbling of liquid-filled elastic capsules in shear flow. *Phys Rev E* 2008;**77**:016310.
6. Walter J, Salsac A-V, Barthès-Biesel D, Ellipsoidal capsules in shear flow: prolate versus oblate initial shapes. *J Fluid Mech* 2011;**676**:318-347.
7. Keller SR, Skalak R, Motion of a tank-treading ellipsoidal particle in a shear flow. *J Fluid Mech* 1982; **120**:27-47.
8. Bagchi P and Kalluri RM, Dynamics of non-spherical capsules in shear flow. *Phys Rev E* 2009;**80**:016307.
9. Foessel É, Walter J, Salsac A-V, Barthès-Biesel D, Influence of internal viscosity on the large deformation and buckling of a spherical capsule in a simple shear flow. *J Fluid Mech* 2011;**672**:477-486.
10. Pozrikidis C, Effect of membrane bending stiffness on the deformation of capsules in simple shear flow. *J Fluid Mech* 2001;**440**:269-291.
11. Sui Y, Chew Y, Roy P, Chen XB, Low HT, Transient deformation of elastic capsules in shear flow: Effect of membrane bending stiffness. *Phys Rev E* 2007;**75**:066301.
12. Le DV, Effect of bending stiffness on the deformation of liquid capsules enclosed by thin shells in shear flow. *Phys* Rev *E* 2010;**82**:016318.
13. Lac E, Barthès-Biesel D, Deformation of a capsule in simple shear flow: Effect of membrane prestress. *Phys of Fluids* 2005;**17**:072105.
14. Barthès-Biesel D, Diaz A, Dhenin E, Effect of constitutive laws for two-dimensional membranes on flow-induced capsule deformation. *J Fluid Mech* 2002;**460**:211-222.
15. Lac E, Barthès-Biesel D, Pelekasis N, Tsamopoulos J, Spherical capsules in three-dimensional unbounded Stokes flows: effect of the membrane constitutive law and onset of buckling. *J Fluid Mech* 2004;**516**:303-334.
16. Walter A, Rehage H, Leonhard H, Shear induced deformation of microcapsules: shape oscillations and membrane folding. *Colloid and Surfaces A* 2001; **183-185**:123-132.
17. Koleva I, Rehage H, Deformation and orientation dynamics of polysiloxane microcapsules in linear shear flow. *Soft Matter* 2012;**8**:3681.
18. Barthès-Biesel D, Modeling the motion of capsules in flow. *Curr Opin Colloid Interface Sci* 2011;**16**:3-12.
19. Abkarian M, Faivre M, Viallat A, Swinging of Red Blood Cells under Shear Flow. *Phys Rev Lett* 2007;**98**:188302.
20. Ramanujan S, Pozrikidis C, Deformation of liquid capsules enclosed by elastic membranes in simple shear flow: large deformations and the effect of fluid viscosities. *J Fluid Mech* 1998;**361**:117-143.
21. Kessler S, Finken R, Seifert U, Swinging and tumbling of elastic capsules in shear flow. *J Fluid Mech* 2008;**605**:207-226.
22. Sui Y, Chew YT, Roy P, Cheng YP, Low HT, Dynamic motion of red blood cells in simple shear flow. *Phys of Fluids* 2008;**20**:112106.
23. Yazdani A, Bagchi P, Influence of membrane viscosity on capsule dynamics in shear flow. *J Fluid Mech* 2013;**718**:569-595.
24. Skotheim JM, Secomb TW, Red Blood Cells and Other Nonspherical Capsules in Shear Flow: Oscillatory Dynamics and the Tank-Treading-to-Tumbling Transition. *Phys Rev Lett* 2007;**98**:078301.
25. Brook MA, *Silicon inorganic, organometallic and polymer chemistry.* 1st ed. New York: Wiley; 2000.
26. Koleva I, *Untersuchung der mechanischen Eigenschaften von Polysiloxan-Membranen und der Deformations- und Orientierungsdynamik von Polysiloxanmikrokapseln im Scherfeld*. Dissertation; Dortmund: 2011.
27. Mezger TG, *Das Rheologie Handbuch*. 2nd ed. Hannover: Vincentz; 2006.
28. Koleva I, Rehage H, A comparison of different experimental methods for investigating the mechanical properties of plane polysiloxane membranes and capsules walls. *Soft Matter* 2012;**8**:7672-7682.
29. Barthès-Biesel D, Role of interfacial properties on the motion and deformation of capsules in shear flow. *Physika A* 1991;**172**:103-124.
30. Abkarian M, Viallat A, Dynamics of Vesicles in a Wall-Bounded Shear Flow. *Biophys J* 2005;**89**:1055-1066.
31. Finken R, Seifert U, Wrinkling of microcapsules in shear flow. *J Phys Condens Matter* 2006;**18**:L185-L191.
32. Knoche S, Vella D, Aumaitre E, Degen P, Rehage H, Cicuta P, Kierfeld J, Elastometry of Deflated Capsules: Elastic Moduli from Shape and Wrinkle Analysis. *Langmuir* 2013;**29**:12463-12471.
33. Dupire J, Socol M, Viallat A, Full dynamics of a red blood cell in shear flow. *PNAS* 2012;**109**:20808-20813.
34. Husmann, M, Rehage H, Dhenin E, Barthès-Biesel D, Deformation and bursting of non-spherical polysiloxane microcapsules in a spinning drop apparatus. *J Colloid Interface Sci* 2005;**282**:109-119.