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LETTER TO THE EDITOR

Wrinkling of microcapsules in shear flow

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Abstract
Elastic capsules can exhibit short wavelength wrinkling in external shear flow. We analyse this instability of the capsule shape and use the length scale separation between the capsule radius and the wrinkling wavelength to derive analytical results both for the threshold value of the shear rate and for the critical wavelength of the wrinkling. These results can be used to deduce elastic parameters from experiments.

The pronounced shape transformations of vesicles and microcapsules induced by hydrodynamic flow paradigmatically illustrate a main theme in microfluidics. The dynamical balance between fluid-induced viscous and membrane-determined elastic stresses depends crucially and distinctively on the specific soft object immersed into the flow. In shear flow, *fluid* bilayer vesicles assume a stationary tank-treading shape if there is no viscosity contrast between the interior and exterior fluid [1]. If the interior fluid or the membrane gets more viscous, a transition to a tumbling state can occur [2–7]. While comprehensive experiments are still lacking, tank-treading has been observed both for vesicles in infinite shear flow [8] and, in particular, for vesicles interacting with a rigid wall [9, 10] where a dynamical lift occurs [11–14]. For a comprehensive review of the dynamical behaviour of soft capsules in shear flow, we refer the reader to the first two chapters of [15].

In contrast to fluid vesicles, genuine microcapsules exhibit a finite shear rigidity since their membrane is physically or chemically cross-linked. While shear elasticity prevents very large shape transformations such as a prolate–oblate transition in fluid vesicles [5], it also leads to qualitatively different instabilities in shear flow like the wrinkling instability first observed experimentally [16]; see figure 1. In fact, wrinkling is a ubiquitous phenomenon which can occur whenever a compressive force acts on a thin sheet either clamped at boundaries or attached to an elastic substrate as happens for the wrinkling of skin [17, 18].

The quantitative study of wrinkling is challenging since the usually large deformations of thin sheets lead to nonlinear partial differential equations for the force balance. Still, rather general statements about wrinkling phenomena become possible, since the nonlinearity is mostly due to geometric effects and thus universal. Indeed, it has been pointed out by Cerda

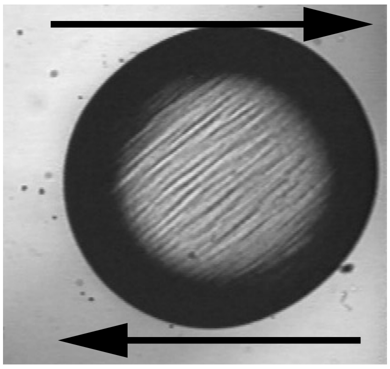

Figure 1. Wrinkling of a polysiloxane capsule ($\simeq$343 μm) in shear flow as indicated by the arrows (adapted from [16]).

et al in a series of intriguing papers [17–19] that geometry puts such a strong constraint on the underlying physics that wrinkles which form in very different contexts all obey the same scaling laws. They consequently identified as the necessary ingredients for all wrinkling phenomena a thin sheet with a bending stiffness, an effective elastic foundation, and an imposed compressive strain [18]. These ingredients give rise to a rather general effective Hamiltonian description, where long wavelength wrinkles are punished energetically due to the increasing longitudinal stretching strain, while short wavelength wrinkles increase the bending energy. This leads to the selection of the optimal wrinkling wavelength.

Since Cerda *et al* considered universal scaling behaviour of all wrinkling phenomena, conversely no conclusions concerning the physical origin underlying the effective constants can be drawn from the scaling behaviour alone. Considering the elastic capsule system in particular, identifying the effective elastic stiffness of the rather complex coupled fluid–membrane system is not trivial. Moreover, the Hamiltonian description is *a priori* no longer valid when the compressive forces acting on the membrane are nonconservative in nature, e.g. when arising from a *hydrodynamic* flow. Here, dynamical effects have to be taken into account. In this letter we therefore complement the approach discussed above by taking advantage of the short wavelength of the observed wrinkles. We can thus identify a new mechanism by which short wavelength wrinkles are selected in a *curved geometry*. This approach can also be generalized to the full dynamic problem, although we have so far only taken into account the short-time dynamics. Moreover, the exact asymptotic limit allows us to make quantitative (i.e. non-scaling-argument) predictions on the onset and direction of wrinkles.

Assuming linear elasticity (and presupposing the capsule was initially stress-free) the work required to deform the membrane is given by the expression

$$\mathcal{H}[\mathbf{R}] = \frac{1}{2}\int \mathrm{d}A \left(\lambda\, \mathrm{Tr}(\boldsymbol{\epsilon})^2 + 2\,\mu\boldsymbol{\epsilon}{:}\boldsymbol{\epsilon} + \kappa\left(2H - \frac{2}{R}\right)^2\right). \tag{1}$$

Here λ is the two-dimensional isotropic compressibility, μ the Lamé coefficient corresponding to the shear stress, and κ the bending modulus of the elastic material, for which we assume for simplicity a spontaneous curvature given by the initial capsule radius. The resulting forces can be calculated as functional derivatives of the energy with respect to the deformation $\mathbf{f}^{\mathrm{el}} = -\delta\mathcal{H}[\mathbf{R}]/\delta\mathbf{R}$. We now immerse this capsule of radius R into a fluid of viscosity η subject to the unperturbed shear flow

$$\mathbf{v}^{\infty} = \dot{\gamma}[(y/2)\mathbf{e}_x + (x/2)\mathbf{e}_y], \tag{2}$$

where $\dot{\gamma}$ denotes the shear rate. (Here x and y refer to global Cartesian coordinates fixed in a laboratory frame.) Considering more general linear shear flow is straightforward, but would distract from the wrinkling problem. For the system at hand the resulting Reynolds number of the flow is negligible, so that the velocity field $\mathbf{v}$ and pressure p are governed by the Stokes equation $\eta\Delta\mathbf{v} = \nabla p$ together with the incompressible continuity equation $\nabla\cdot\mathbf{v} = 0$. With the definition of the hydrodynamic stress $\boldsymbol{\sigma} = -p\mathbf{1} + \eta\left[\nabla\mathbf{v} + (\nabla\mathbf{v})^{\mathrm{T}}\right]$ the Stokes equation can also be written as $\nabla\cdot\boldsymbol{\sigma} = 0$. The hydrodynamic force acting on the membrane is given by $\mathbf{f}^{\mathrm{fl}} \equiv [\boldsymbol{\sigma}\cdot\mathbf{n}]_{\mathrm{in}}^{\mathrm{out}}$. The Stokes equations are accompanied by the asymptotic boundary condition $\mathbf{v}(\mathbf{r}) \to \mathbf{v}^{\infty}$ for $|\mathbf{r}| \to \infty$, the force balance $\mathbf{f}^{\mathrm{el}} + \mathbf{f}^{\mathrm{fl}} = 0$ at the membrane, and the kinematic condition that the membrane is convected by the fluid, $\mathbf{v}|_{\mathbf{R}(\theta,\phi,t)} = \partial_t\mathbf{R}(\theta,\phi,t)$.

These equations fully determine the evolution of the capsule shape. Unfortunately, they are highly nonlinear and non-local, so that a solution is only possible numerically or in certain asymptotic limits. Let us now suppose that we have found a stationary solution, and look for the stability of small perturbations $\delta\mathbf{r}$ of the membrane position. From the experimental evidence [16] it is expected that beyond a critical shear rate $\dot{\gamma}_{\mathrm{c}}$ the stationary deformation becomes unstable with respect to the formation of short wavelength wrinkles. For a first qualitative discussion, we consider a given configuration with known initial strain tensor $\boldsymbol{\epsilon}_0$ and impose oscillatory wrinkles perpendicular to the membrane with the large wavevector $k\mathbf{e}_x$, leading to $\delta\mathbf{r} = \delta r\cos(kx)\mathbf{e}_z$. In this one-dimensional picture, the strain is simply the relative change in length of a line element with respect to a reference element. An initially straight line (a cut through a *flat* membrane) always increases in length when folded. The relative length change is of the order $\delta l_1/l \sim (\delta r)^2k^2$. This effect is of second order in the amplitude and grows quadratically with the wavenumber. For a *curved* membrane, there is an additional first order length change $\delta l_2/l \sim \delta r\cos(kx)/R$, arising from the fact that the local curvature radius of the line is periodically displaced outward and inward. Both contributions are added to the initial strain. For the *curved* membrane, the relevant component of the strain tensor thus changes to

$$\epsilon \sim \epsilon_0 + (\delta r)^2k^2 + \delta r\cos(kx)/R. \tag{3}$$

Even though the curvature induced part is oscillatory and vanishes in the mean, it nevertheless gives rise to a positive contribution in the elastic energy, which is quadratic in the strain. For large wavenumbers, the local curvature, which is of the order $k^2\delta r$, gives rise to the most important contribution to the total energy. After averaging over the fast oscillations, one obtains for the elastic energy (ignoring pre-factors of order unity and the shear elasticity for a moment)

$$\mathcal{H}^{\mathrm{el}} \sim \mathcal{H}_0^{\mathrm{el}} + \int \mathrm{d}A\,\frac{\lambda}{R^2}(\delta r)^2 + \lambda\epsilon_0(\delta r)^2k^2 + \kappa(\delta r)^2k^4. \tag{4}$$

This expression has formally the same form as the effective Hamiltonian in [18], so that we can identify the bending stiffness κ, the stress $\lambda\epsilon_0$, and the effective elastic foundation stiffness λ/R^2. Before we discuss the latter quantity in more detail, let us briefly recapitulate how these terms lead to short wavelength wrinkling for sufficiently large compressive stress. For an initially compressed membrane (i.e. $\epsilon_0 < 0$), the compressive stress is partially cancelled by the second order contribution $(\delta r)^2k^2$. This lowers the modulus of the resulting stress and therefore decreases energy. This mechanism is also the driving force for Euler buckling of planar membranes and rods. For a curved membrane, there is an additional contribution that always serves to increase the elastic energy. Only with a sufficiently large compressive pre-strain ($\epsilon_0 < 0$) is one able to overcome this energy cost. Since the energy gain is quadratic in the wavenumber, short wavelength wrinkles will overcome the cost associated with the curvature effect sooner for increasing $|-\epsilon_0|$. However, very large wavenumbers are penalized by the bending energy. A simple discussion of the functional form (4) thus reveals that gaining elastic energy by wrinkling is possible provided that the initial compressive stress exceeds a threshold $\tau_0 = \lambda|\epsilon_0| > \tau_c \sim \sqrt{\lambda\kappa}/R$. Even though this scaling prediction is already implicit in [18], the $1/R$ term shows the crucial influence of a curved geometry here.

This critical stress must be provided by the imposed hydrodynamic flow. From a simple dimensional analysis one can deduce that this stress is of the order $\tau \sim \eta\dot{\gamma}R$. For the critical stress we find a critical shear rate $\dot{\gamma}_c \sim \sqrt{\kappa\lambda}/(\eta R^2)$ and a critical wrinkling wavenumber $k_c \sim (\lambda/(\kappa R^2))^{1/4} \sim 1/(hR)^{1/2}$, where the second relation arises when we treat the membrane as an isotropic shell of thickness h and bulk modulus E, i.e. $\lambda \sim Eh$ and $\kappa_c \sim Eh^3$.

This discussion reveals the physical origin of the effective stiffness λ/R^2: Any normal deformation on a *curved* membrane leads to an additional strain contribution that increases the elastic energy to second order in the amplitude. This picture becomes more subtle when we allow the membrane to relax tangentially: in plane displacements will reduce the second order strain to minimize its energy contribution. The two dimensional freedom in general does not allow us to reduce the full stress tensor, which consists of three independent components, to zero. This becomes possible, however, for particular values of the material constants or the membrane geometry. If the shear modulus of the membrane vanishes, tangential deformations can completely eliminate the isotropic strain. In such a membrane the effective stiffness consequently vanishes. This explains why wrinkling is not observed for fluid membranes. When the curvature perpendicular to the wrinkle wavevector vanishes, it again becomes possible to eliminate the total additional stress. Thus the wrinkling phenomenon on a capsule necessarily needs both a curved geometry and finite values for the compressibility and shear modulus.

The quantitative treatment is considerably more complicated. We not only have to express the change in the elastic energy due to wrinkling not necessarily perpendicular to the membrane on a quantitative level, but we also have to take the change in the hydrodynamic forces due to the deformed capsule into account, since change in the forcing linear in the amplitude acts on the same level as the quadratic change of the elastic energy. However, we can neglect all these complications if we assume that the number of wrinkles on the membrane, $k_c R$, is large. Formally, we are looking for the singular perturbation solution of the dynamic equations in the limit $\varepsilon \equiv (\kappa/(\lambda R^2))^{1/4} \sim 1/(k_c R) \to 0$. When we compare the elastic forces with the change in the hydrodynamic forces in detail, we find that the latter can be ignored as being of the order ε.

We now turn to the *quantitative* predictions. The wrinkling pattern is assumed to be of the more general form $\delta\mathbf{r} = \delta\mathbf{r}_0 \exp(\mathrm{i}\Theta)$, where the local wavevector is now given as the gradient of the phase $\mathbf{k} \equiv \nabla\Theta$. The amplitude $\delta\mathbf{r}_0$ and the wavevector $\mathbf{k}$ are allowed to vary slowly on the membrane. The collection of the most important contributions to the change in elastic energy is formally obtained via WKB theory [20]. We need to consider non-normal deformations of the membrane, which allows the membrane to reduce the stress even further. We will publish the details of the calculation elsewhere and only note that the energy change due to the formation of wrinkles on a sphere is

$$\delta^2\mathcal{H} = \frac{1}{4}\int \mathrm{d}A \left\{4\mu\frac{\lambda+\mu}{\lambda+2\mu}\frac{1}{R^2} + \mathbf{k}\cdot\boldsymbol{\tau}\cdot\mathbf{k} + \kappa|k|^4\right\}\delta r^2. \tag{5}$$

Here $\boldsymbol{\tau}$ denotes the tangential part of the elastic stress tensor, which is effectively a symmetric 2×2 matrix determined by the external forces. When this matrix has a sufficiently large negative eigenvalue, energy can be gained from the formation of wrinkles. The force driving the folding is the negative derivative of (5) with respect to δr and in this order linear in the amplitude. The elastic forces in turn induce a flow in the surrounding fluid that convects the

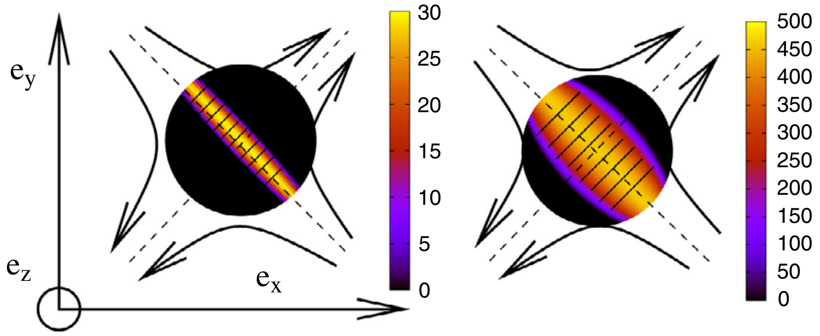

Figure 2. Wrinkling instability region for $\dot{\gamma} = 11.5\ \mathrm{s}^{-1}$ (left) and $\dot{\gamma} = 17.0\ \mathrm{s}^{-1}$ (right), respectively. The elastic moduli of the membrane are $\lambda = \mu = 0.1\ \mathrm{N\ m}^{-1}$, $\kappa = 1 \times 10^{-17}$ N m. In the black coloured region the membrane is still stable with respect to wrinkle formations. Brighter colours indicate a larger growth rate of the wrinkles. Initially wrinkling occurs only in a small region around the circumference corresponding to the plane of maximal compressive stress. At higher shear rates this region grows, as does the growth rate of each wrinkling mode. The direction of the wrinkles along the lines of maximal tension are indicated schematically.

(This figure is in colour only in the electronic version)

membrane points. In general, this effect would be non-local, leading to a coupling between the wrinkling dynamics at different points of the capsule. However, at zero order in the asymptotic short wavelength limit the hydrodynamic effects are local and diagonal in the coordinate system adapted to the membrane. We are thus led to the evolution equation

$$\partial_t(\delta r) = -\frac{1}{8\eta|k|}\left\{\frac{4\mu}{R^2}\frac{\lambda+\mu}{\lambda+2\mu} + \mathbf{k}\cdot\boldsymbol{\tau}\cdot\mathbf{k} + \kappa|k|^4\right\}\delta r \equiv \frac{\delta r}{\tau}, \tag{6}$$

which implies a timescale τ for the short time dynamics of each wrinkling mode. We take the time constant as a measure of the strength of the instability and assume that locally the fastest growing mode is dynamically selected. We can thus find the resulting folding pattern by maximizing the rhs of equation (6). Note that the only input needed for this theory is the initial stress distribution $\boldsymbol{\tau}$, which is caused by the hydrodynamic flow. For general shapes, these data can come e.g. from numerical simulations such as [5]. For the present purpose, we will use analytic results for the expansion of the stress to first order in the shear rate $\dot{\gamma}$ [21]. The stress distribution on a stationary sphere in linear shear flow (2) is independent of the material constitutive law and reads in spherical coordinates, see figure 2,

$$\boldsymbol{\tau} = \begin{pmatrix} \tau_{\theta\theta} & \tau_{\theta\phi} \\ \tau_{\phi\theta} & \tau_{\phi\phi} \end{pmatrix} = \dot{\gamma}\tfrac{5}{2}\eta R \begin{pmatrix} \sin 2\phi & \cos 2\phi\cos\theta \\ \cos 2\phi\cos\theta & -\sin 2\phi\cos^2\theta \end{pmatrix}. \tag{7}$$

The wavevector field of the wrinkles is given by the direction of the negative eigenvalues of (7). Even though these can be calculated analytically, they are given by rather involved expressions. However, one can see that the most negative stress eigenvalue $-5\dot{\gamma}\eta R/2$ appears along the circumference $\phi = 3\pi/4, 7\pi/4$, which is at angle $\pi/4$ with the shear direction. The corresponding eigenvector points perpendicular to this circumference along the θ coordinate lines. Along this circumference the local compression is maximal, from which we can calculate the critical shear rate $\dot{\gamma}_c$ and the corresponding critical wavenumber k_c analytically as

$$\dot{\gamma}_c = \frac{8}{5\eta R^2}\sqrt{\mu\kappa\frac{\lambda+\mu}{\lambda+2\mu}} = \frac{4\kappa}{5\eta R}k_c^2. \tag{8}$$

These two expressions are our main quantitative results. The scaling is of course the same as predicted in [18]. However, we also predict quantitative prefactors that become exact in the large wavenumber limit. Above the critical shear rate $\dot{\gamma}_c$ wrinkles start to form in a finite region starting uniformly along the circumference $\phi = 3\pi/4, 7\pi/4$. With increasing shear rates this wrinkling region grows symmetrically towards the stagnation points of the flow located at $\theta = \pi/2, \phi = \pi/4, 5\pi/4$. The wrinkling direction is determined by the direction of the eigenvectors of the stress tensor. Along the initial wrinkling circumference, the folds form perpendicular to this line, i.e. in the direction of maximal tension, in accordance with experimental findings [16].

Inserting experimental value for the planar elastic moduli [16] $\lambda \simeq \mu \simeq 0.1$ N m^{-1} and counting the number of wrinkles across the membrane (cf figure 1) we arrive at an estimate for the bending rigidity $\kappa \simeq 1 \times 10^{-17}$ N m, in accordance with a similar estimate made in [18]. Of course, due to the fourth power taken, the estimation for κ (cf equation (8)) depends sensitively on the measured wavenumber. For these values, together with the capsule radius $R \simeq 343$ μm and the viscosity of water, $\eta = 10^{-3}$ Pa s, the critical shear rate is predicted to be $\dot{\gamma}_c \sim 11$ s^{-1}. This value is in good agreement with the experimentally reported onset at $\dot{\gamma}_c \simeq 4$ s^{-1} [16]. For shear rates larger than $\dot{\gamma}_c$, the minimization of (6) is best performed numerically. The growth of the wrinkling region for the numerical shear rates $\dot{\gamma} = 11.5$ s^{-1} and $\dot{\gamma} = 17.0$ s^{-1} is shown in figure 2.

In conclusion, we have presented an analytical theory for the wrinkling instability of a microcapsule in shear flow. This was accomplished by a systematic singular perturbation expansion in the bending rigidity. The only input needed, apart from the material constants, is the initial stress distribution. For quasispherical capsules all quantities can be calculated explicitly, leading to analytical expressions of the shear rate and the wrinkling wavelength at the onset. This provides a method to deduce the bending rigidity from shear experiments. Given the relatively large error in the experimental values of the compressibility, the agreement of the predicted critical shear rate (deduced from the observed wavelength) with experimental values is surprisingly good.

Finally we remark that an initial stress on the membrane (e.g. due to osmotic pressure) affects the critical shear rate. While the effect of membrane prestress on the deformation of capsules has been discussed [22], the effect on the formation of wrinkles has not yet been considered. Since wrinkling can only occur for membranes with shear stress resistance, fluid membrane capsules do not form wrinkles. Thus a study of viscoelastic membranes, which exhibit fluid or elastic behaviour depending on the timescale, seems worthwhile.

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