Wrinkling of Vesicles during Transient Dynamics in Elongational Flow

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Recent experiments by Kantsler *et al.* [Phys. Rev. Lett. **99**, 178102 (2007)] have shown that the relaxational dynamics of a vesicle in external elongation flow is accompanied by the formation of wrinkles on a membrane. Motivated by these experiments we present a theory describing the dynamics of a wrinkled membrane. The formation of wrinkles is related to the dynamical instability induced by negative surface tension of the membrane. For quasispherical vesicles we perform analytical study of the wrinkle structure dynamics. We derive the expression for the instability threshold and identify three stages of the dynamics. The scaling laws for the temporal evolution of wrinkling wavelength and surface tension are established, confirmed numerically, and compared to experimental results.

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Wrinkling of thin sheets is a well-known effect which can be frequently observed in everyday life. Usually wrinkle patterns appear due to the external tensions applied to the material, or as a result of compression of inextensible films. Main properties of steady and/or equilibrium wrinkling structures are now well understood [1]. However, much less is known about the dynamics of wrinkle structures. In certain biologically motivated experiments on membranes and vesicles [2,3], the wrinkles are formed because of the instability induced by negative membrane tension, which is closely related to a buckling instability. These wrinkles exhibit nontrivial growth and relaxational dynamics. Theoretical description of these essentially nonequilibrium processes is a challenging problem which we attempt to approach in this Letter. Although we focus on the analysis of the recent experiments [2], some predictions of our theory are universal and may be successfully applied to other systems where the formation of wrinkles is caused by negative tension.

Vesicles exhibit a variety of different regimes of motion in stationary fluid flows. These regimes were extensively studied during the last decade both experimentally and theoretically (see, e.g., [4–11] and references therein). It was shown that depending on the external parameters a vesicle in external shear flow can experience several different types of motions, such as tank treading, tumbling, and others. Although these regimes of motion correspond to quite nontrivial dynamics, the shape of a vesicle remains smooth and can be effectively approximated by an ellipsoid. Recently, experiments performed by Kantsler *et al.* [2] revealed a qualitatively new effect observed in nonstationary elongation flows. It was shown that in strong flows the relaxational dynamics of a vesicle is accompanied by the excitement of high-order membrane deformation modes called wrinkles. Such dynamics cannot be described in a framework of low-dimensional models used for the analysis of tank treading, tumbling, and trembling, where the vesicle state was described by one or two degrees of freedom. In this Letter we extend these models to include the interaction between the vesicle shape and the wrinkle structure.

Before proceeding further we would also like to mention the experimental [12] and theoretical [13] investigations of wrinkle formation on microcapsules in external shear flows. Although this effect is similar to the one discussed here the underlying physics and main properties of wrinkles are essentially different. For example, the wrinkles which are observed on vesicles are not stationary and are excited only for a limited amount of time.

This Letter is organized as follows: first we discuss the main features of a vesicle and show that the negative tension leads to instabilities of the flat membrane. Second, we present a model of a quasispherical vesicle in external flow. We derive the threshold of the instability and analyze the dynamics of wrinkle formation in strong flows. We show that one can distinguish three different stages of the dynamics. We describe the dynamics during these stages and find the scaling estimations for the wrinkle wavelength and the surface tension and perform a comparison with the experiment. In the end of the letter we compare our results to numerical simulations and experiment.

Vesicles are closed lipid bilayers which are incompressible and impermeable to the surrounding liquid. These two properties result in the conservation of the vesicle volume and the membrane area. Thus any vesicle is characterized by its excess area Δ which is the measure of vesicle's "nonsphericity": $A = (4\pi + \Delta)R^2$, where A is the membrane area and R is the effective vesicle radius, defined by the vesicle volume: $V = 4\pi R^3/3$. Free energy of the closed membrane is defined by the Helfrich functional and consists of the contributions from the bending energy and the surface tension σ [14]:

$$F = \int dA\left(\frac{\kappa}{2}H^2 + \sigma\right). \quad (1)$$

Here H is the local mean curvature and κ is the bending rigidity of a membrane. Note that for closed membrane geometry, the surface tension σ is a quantity adjusting to other membrane parameters (similar to the pressure in an incompressible fluid) to ensure a given value of the membrane area A. It is useful to analyze the stability of a flat membrane with a given value of σ before proceeding to the case of a closed membrane with a fixed area. Small perturbations of a flat membrane can be parametrized by a height function $z = h(x, y)$ which can be expanded in Fourier harmonics: $h(\mathbf{r}) = \sum h_{\mathbf{k}} \exp(i\mathbf{k} \cdot \mathbf{r})$. The quadratic part of the Helfrich energy has the following form:

$$F = \frac{1}{2}\sum_{\mathbf{k}}(\kappa k^4 + \sigma k^2)|h_{\mathbf{k}}|^2. \qquad (2)$$

For positive σ, this function is minimized by $u = 0$, so the flat membrane state is stable. However, for negative tension $\sigma < 0$, when the membrane is being shrunk, the modes with $k < \sqrt{|\sigma|/\kappa}$ become unstable. As we will show, this particular kind of instability is responsible for the formation of wrinkles in the experiment [2].

In order to study this effect quantitatively we use the model of quasispherical ($\Delta \ll 1$) vesicles which proved itself to be very successful in analytical investigations of vesicle dynamics in external flows [7,9–11]. The vesicle shape is parametrized by the small displacement function $u(\theta, \phi)$: $r = R(1 + u)$ which can be expanded in the series of spherical harmonics:

$$u(t, \theta, \phi) = \sum_{lm}\left[\frac{\Delta}{(l-1)(l+2)}\right]^{1/2} u_{lm}(t)\mathcal{Y}_{lm}(\theta, \phi). \qquad (3)$$

The external velocity is assumed to be planar and to have a linear elongational profile with the time-dependent strain: nonzero velocity gradient components are $\partial_x V_y = \partial_y V_x = 11\sqrt{5}/(16\sqrt{6\pi})S(t)\sqrt{\Delta}/\tau$, where $\tau = \eta R^3/\kappa$ is the characteristic time scale associated with the membrane bending forces. The numerical factor in this definition was included to simplify the expressions below. Throughout the Letter we will discuss the experimentally interesting situation when $S(t)$ is the Heaviside-like function $S(t) = -S\,\mathrm{sign}(t)$.

The dynamical equations describing the dynamics of a quasispherical vesicle in external flow were first derived in [7] in the leading order in the small parameter $\sqrt{\Delta} \ll 1$:

$$\tau \dot{u}_{lm} = S(t) f_{lm} - (A_l\sigma + \Gamma_l)u_{lm} + \zeta_{lm}(t). \qquad (4)$$

Here $f_{lm} = \delta_{l,2}(\delta_{m,2} + \delta_{m,-2})$ and $\sigma(t)$ is the dimensionless angularly averaged part of the surface tension which is a Lagrangian multiplier associated with the excess area conservation constraint $\sum |u_{lm}|^2 = 2$. The numerical coefficients of (4) are given by: $\Gamma_l = (l-1)l^2(l+1)^2(l+2)/(2l+1)(2l^2+2l-1)$, and $A_l = l(l+1) \times (l^2+l-2)/(2l+1)(2l^2+2l-1)$. The statistical properties of thermal Langevin forces $\zeta_{lm}(t)$ can be found in [7]. To keep the analysis simple we neglect the contribution from thermal noise terms $\zeta_{lm}(t)$ in the dynamical equation, but assume that the initial conditions for u_{lm} are determined by the stationary statistical distribution which is produced by random thermal forces. We check the validity of such an approximation by numerical simulations of Eqs. (4) with finite temperature.

Stationary shape of a vesicle in an external elongational flow is almost ellipsoidal. Most of the excess area is stored in $\mathcal{Y}_{2,\pm 2}$ harmonics. After the flow direction switching at $t = 0$ the surface tension σ becomes negative and high-order harmonics are excited. The value of the surface tension can be found from the conservation law $\partial_t \sum |u_{lm}|^2 = 0$ and the dynamical Eqs. (4). After substituting $\dot{u_{lm}}$ from (4) and neglecting the thermal noises we obtain a linear equation for σ whose solution is given by

$$\sigma = \frac{S(t)\mathrm{Re}[u_{2,2}] - \bar{\Gamma}}{\bar{A}}, \qquad (5)$$

where we introduced the average values $\bar{A} = \sum_l A_l \Delta_l$ and $\bar{\Gamma} = \sum_l \Gamma_l \Delta_l$ and the spectral distribution of the excess area $\Delta_l = \sum_m |u_{lm}|^2$. Using the expression (5) one can easily show that there will be an instability for large enough values of S. Indeed, for constant positive $S(t) = S$ at $t < 0$ the stationary shape of a vesicle corresponds to $u_{2,2} = 1$. However, as $S(t)$ changes sign this state becomes unstable and the vesicle begins its rotation to the new stable point which corresponds to $u_{2,2} = -1$. The stability of the membrane is determined by the sign of σ given by (5). The surface tension instantly becomes negative after changing the velocity field: $\sigma(t = +0) = -(\Gamma_2 + S)/A_2$. From (4) we find that all harmonics of order up to l become unstable if $A_l\sigma + \Gamma_l < 0$, which yields $S > S_l = A_2\Gamma_l/A_l - \Gamma_2$. For $l \gg 1$ one obtains $S_l \sim A_2 l^2 \gg 1$. The most unstable mode can be found by maximizing the growth increment $-\Gamma_l - A_l\sigma$ which yields $l_0 = \sqrt{S/3A_2}$ for strong flows with $S \gg 1$. Third order harmonic becomes unstable for $S > S_3 = 1.8$.

Below the instability threshold for small values of S, higher order harmonics are not excited and the dynamics of a vesicle can be well described in terms of one complex variable $u_{2,2} = |u_{2,2}|e^{-2i\Phi}$, where Φ is vesicle orientation angle in xy plane. The conservation of excess area implies that the dynamics is purely rotational, $|u_{2,2}| = 1$, and the evolution of $\Phi(t)$ is described by the equation $\tau\dot{\Phi} = -S\cos 2\Phi$. The characteristic time scale associated with the rotational dynamics is estimated as τ/S.

Describing the dynamics of the vesicle above the instability threshold is a considerably more difficult problem which requires an analysis of a nonlinear system (4) with large number of degrees of freedom. Fortunately, it is possible to approach this problem analytically for strong flows which correspond to $S \gg 1$. In this case one can distinguish between several different stages in the wrinkle evolution. The formal solution of (4) is given by

$$u_{lm}(t) = u_{lm}(0)\exp(-\Gamma_l t/\tau + A_l\rho) \qquad (6)$$

for high harmonics $l \geq 3$, where $\rho = -\int_0^t dt' \sigma(t')/\tau$ is the solution of the equation $\tau\dot{\rho} = -\sigma$ with σ given by (5). During the first stage of the dynamics most of the excess area is stored in the second-order angular harmonics and the surface tension is almost constant $\sigma = -2S/A_2$. Unstable high-order harmonics grow exponentially fast and the distribution of excess area $\Delta_l = \sum_m |u_{lm}|^2$, $l \geq 3$, becomes centered near the most unstable modes with $l = l_0 \sim \sqrt{S}$. One could naïvely expect that l_0 would determine the characteristic length of the wrinkles which are observed in the experiments. This, however, is not the case. Rapid exponential growth saturates when the total excess area, stored in high-order harmonics, becomes large enough so that their contribution to the surface tension (5) becomes comparable to the contribution from the external flow. After that moment the surface tension becomes a time-dependent decreasing function and such becomes the center of the excess area distribution. Formal condition can be found from (5) and expression for l_0: $(1 - |u_{2,2}|^2) \sim S^{-1/2} \ll 1$. Note that at this moment most of the excess area is still stored in the second-order harmonic. The characteristic duration of the first stage can be estimated from (4) assuming that the initial value $u_{lm}(0)$ has a characteristic value which is determined by the stationary distribution: $\langle |u_{lm}|^2 \rangle \sim 2T/\kappa(l^4 + Sl^2/A_2)$ [7]. This yields the following estimation: $\tau_1 \sim \tau S^{-3/2} \ln[S^{1/4}\kappa/T]$. Below we assume that $S^{1/4} \gg T/\kappa$. Note that the duration of the first stage is much smaller than the characteristic relaxation time of the second-order harmonics, which can be estimated as τS^{-1}.

Second stage starts at $t \gtrsim \tau_1$ after the exponential growth has saturated. During this stage the surface tension is determined by distribution of high-order harmonics u_{lm}, $l \geq 3$. Using (5) one can derive the following approximation: $\sigma = -(\bar{\Gamma}/\bar{A})$. The distribution of excess area Δ_l is a narrow function of l centered around some $\bar{l} \gg 1$ which is determined as maximum of the exponent in Eq. (6): $\bar{l} = \sqrt{\rho\tau/3t}$. The characteristic width of the distribution can be estimated as $\delta l \sim (\bar{l}t/\tau)^{-1/2}$. It is small compared to $\bar{l}$ in the case $S^{1/4} \gg T/\kappa$. Narrowness of the Δ_l distribution allows one to find the exact expression for the surface tension: $\sigma = -\bar{\Gamma}/\bar{A} = -\bar{l}^2 = -\rho\tau/3t$. Using the definition of ρ we obtain the following closed equation:

$$\dot{\rho} = \rho/3t. \tag{7}$$

One can find its solution using the initial condition for the surface tension: $\sigma \sim S$ at $t \sim \tau_1$. This yields $\rho = c(t/\tau)^{1/3}$, where $c \sim \log^{2/3}(\kappa S^{1/4}/T)$. Similarly we obtain $\sigma = -(c/3)(t/\tau)^{-2/3}$ and $\bar{l} = \sqrt{c/3}(t/\tau)^{-1/3}$. Therefore, second stage of the dynamics is characterized by the algebraic decay of the surface tension and by the narrow spectral distribution Δ_l of the wrinkling structure, whose peak smoothly drifts towards small l. Physically this drift corresponds to the broadening of the wrinkles. As the absolute value of $\bar{l}$ goes down, the external velocity contribution $S(t)\mathrm{Re}[u_{2,2}]$ to the surface tension in (5) becomes important again. Comparing different contributions in (5) one can estimate the duration of the second stage as τ/S. In the end of the second stage, when the wrinkles amplitude is the highest, the peak of the Δ_l distribution is centered near $l_* \sim S^{1/3}$. This scaling law relates wavelength of wrinkles to the strain $\lambda \sim RS^{-1/3}$ and is one of the main results of this Letter. Note that this wavelength is much smaller compared to the wavelength of the initially most unstable mode which is of order $RS^{-1/2}$. The exponent $1/3$, which characterizes the broadening dynamics of wrinkles, is universal: it does not depend on the details of the vesicle dynamics. One can expect this exponent in any experiment where the strong negative surface tension is produced instantly.

During the third stage, which takes place at $t \gtrsim \tau/S$ the surface tension is determined both by the external velocity and the wrinkles. During this stage the vesicle approaches its new stable state. Although this stage is not universal in the sense explained above, one can derive some results to compare them to experiments or simulations. For instance, the dynamics of the second-order harmonics is driven mainly by the external velocity term $S(t)$. Therefore, in the leading order the evolution of $u_{2,2}(t)$ can be described by the linear law: $u_{2,2}(t) = 1 - St/\tau$. One can see that the time of relaxation to the new stable state is equal to $2\tau/S$ and the characteristic amplitude of wrinkles has the following time dependence: $\sqrt{1-|u_{2,2}|^2} = \sqrt{(2-St/\tau)St/\tau}$. The maximal amplitude can be observed at $t = \tau/S$.

We have tested our results by direct numerical simulations of Eq. (4). The total number of harmonics in our simulations was determined by $l_{\max} \approx 2\sqrt{S}$. We have used different values of temperature, which determines the amplitude of $\zeta_{lm}(t)$ terms in (4). The results of the simulations were almost insensitive to the temperature for $S \gg 1$; however, there was a noticeable difference for $S \approx 1$. In Fig. 1 one can see the results of simulations for some particular values of parameters. Three temporal stages with qualitatively different dynamics are clearly distinguishable. The behavior of Δ_2 is very close to quadratic observed in experiments and predicted by our theory. The dynamics of $\sigma(t)$ may be well fitted by the power law $\sigma \propto t^{-2/3}$ during the second stage.

In Fig. 2 we present the behavior of the characteristic wrinkle wavelength l_* (calculated in the same way as k_* in [2]) as a function of the strain rate S. The limiting slope of the curve for $S \gg 1$ confirms our theoretical prediction $l_* \propto S^{1/3}$. It is also in a reasonable agreement with the results of [2] where the slope $l_* \propto S^{0.25}$ was observed. For weak flows with $S \approx 1$–10 the value of l_* is determined by thermal fluctuations and one has $l_* \approx 5$ similar to the one observed experimentally. Note that the mean wave-

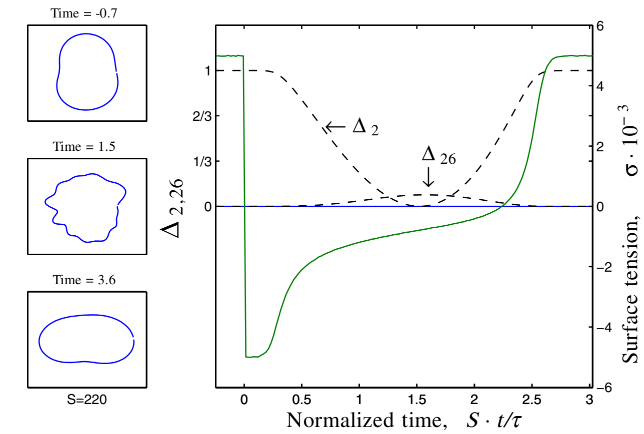

FIG. 1 (color online). Temporal evolution of Δ_2, Δ_{26}, and σ from numerical simulations of (4) with $S = 2 \times 10^3$ and $T/\kappa\Delta = 10^{-4}$. Δ_{26} is the most excited harmonic with $l \geq 3$ in these simulations. On the left: the projections of vesicle on XY plane.

length of dynamically excited wrinkles surpasses thermal equilibrium value at the values of $S = S_c$ which is much larger than the instability threshold. Value S_c in Fig. 2 would correspond to the experimentally observed threshold $S_c \approx 18$ if the real value of membrane rigidity would be $\kappa \approx 1.8 \times 10^{-13}$ erg, which is about 6 times smaller than the one used in the analysis of experiments in [2]. Note also that the dependence on S is not monotonic. There exists a minimum for $S \approx 10$–30. In this range of S third and fourth order harmonics are strongly excited, and they provide the main contribution to the value of l_*. Depth of the minimum depends on the temperature: it almost vanishes for $T/(\kappa\Delta) \approx 1$.

In conclusion, we compile a list of main results presented in this Letter. Motivated by recent experiments [2], we studied the relaxational dynamics of a vesicle in an elongational flow. We have shown that high-order membrane deformation modes are excited by the negative surface tension induced by external flow. For quasispherical vesicles we have found an analytical expression for the instability threshold $S_3 \approx 1.8$ and analyzed the evolution of the wrinkle structure for strong flows. We identified three stages of the dynamics. The first stage corresponds to $t \lesssim \tau_1 = \tau S^{-3/2} \log(S^{1/4}\kappa\Delta/T)$ and is characterized by the exponential growth of unstable high-order harmonics with the characteristic scales of order $\lambda \sim RS^{-1/2}$. This rapid growth quickly saturates and is followed by the second stage. For $\tau_1 \ll t \lesssim \tau/S$ the surface tension decays algebraically as $\sigma(t) \propto t^{-2/3}$ and the characteristic wavelength of wrinkles grows as $\lambda \propto t^{1/3}$. Characteristic amplitude of the wrinkles grows as $\sqrt{t}$. During the third stage which ends at $t = 2\tau/S$ wrinkle amplitude behaves like

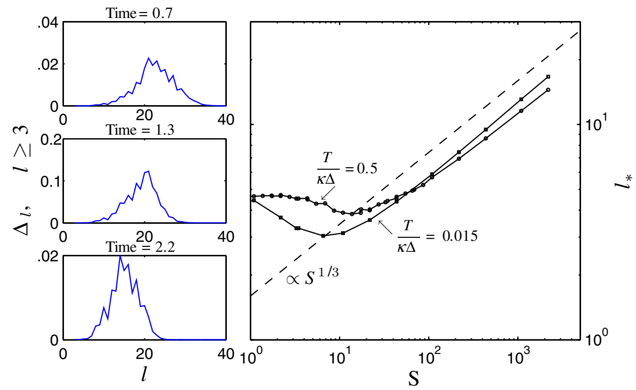

FIG. 2 (color online). Numerical results for the characteristic wrinkles wave number l_* which is defined in the same way as k_* in [2]. On the left: spectral distribution Δ_l at different time moments (from simulations with $S = 10^3$ and $T/\kappa\Delta = 0.015$).

$\sqrt{(2 - St/\tau)St/\tau}$ and the characteristic wavelength can be estimated as $\lambda \sim RS^{-1/3}$.

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