Rheology of a Dilute Suspension of Vesicles

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From the hydrodynamical equations of vesicle dynamics under shear flow, we extract a rheological law for a dilute suspension. This is made analytically in the small excess area limit. In contrast to droplets and capsules, the rheological law (written in the comoving frame) is nonlinear even to the first leading order. We exploit it by evaluating the effective viscosity η_{eff} and the normal stress differences N_1 and N_2. We make a link between rheology and microscopic dynamics. For example, η_{eff} is found to exhibit a cusp singularity at the tumbling threshold, while $N_{1,2}$ undergoes a collapse.

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Simple fluids and elastic solids are described by universal equations, namely, Navier-Stokes and Lamé equations. A derivation of similar laws for complex fluids continues to pose a formidable challenge. Complex fluids include suspensions, emulsions, polymer solutions, blood, and so on. The major challenge for the extraction of a constitutive law lies in the inherent coupling between microscales (represented by the entities suspended in the fluid) and the flow at the global scale. As a consequence, a time scale separation between micro and macrodynamics is not permissible. In the general case no universal constitutive law (if any) is available.

Macroscopic constitutive laws for complex fluids should generally carry information on the microscale, despite the fact that the law represents an averaged property. In principle, a derivation of a constitutive law should emerge from the microscopic knowledge of the dynamics of the suspended entities. The present Letter is directed along this line by focusing on rheology of vesicle suspensions.

The problem of a vesicle under flow has revealed several interesting dynamics such as tank-treading [1], tumbling [2,3], and vacillating-breathing [4] modes, and it continues to hold an increasing amount of interest both theoretically [1–3,5], and experimentally [6]. Besides the understanding of the various intricate dynamics of individual vesicles under nonequilibrium conditions, it is highly desirable to understand their rheological properties.

We perform a homogenization technique to extract the stress tensor at the global scale as a function of the dynamical evolution of the vesicles in the dilute regime. Even to the first leading order, the extracted rheological law (written in the comoving frame) is found to be nonlinear, in marked contrast with droplets and capsules rheology. We make a link between the various dynamics and the overall rheology. In particular, we show that the effective viscosity exhibits a cusp singularity at the tumbling threshold, while the normal stress differences collapse in the tumbling and vacillating-breathing (VB) regimes.

The vesicle suspension is submitted to a linear shear flow $\mathbf{V_0} = (\dot{\gamma} y, 0, 0)$, where $\dot{\gamma}$ is the shear rate. The flow outside (and inside) a vesicle is described by the Stokes equations. Lengths are reduced by the vesicle radius r_0 (r_0 designates the radius of a sphere having the same volume), and time by $\dot{\gamma}^{-1}$. The shape of the vesicle can be written in the general case as an infinite series on the basis of spherical harmonics $\mathcal{Y}_{nm}$

$$r = 1 + \epsilon \sum_{n=0}^{\infty} \sum_{m=-n}^{n} F_{nm}(t) \mathcal{Y}_{nm}(\theta, \phi), \tag{1}$$

where ϵ is a small parameter expressing a small deviation from a sphere, θ and ϕ are the usual angles in spherical coordinates, and $F_{nm}(t)$ is a time-dependent amplitude (to be determined) of the corresponding spherical harmonic. Using the expression of spherical harmonics in terms of Cartesian coordinates, r_i, we have

$$\sum_{m=-2}^{2} F_{2m}(t) \mathcal{Y}_{2m}(\theta, \phi) = \sum_{i,k=x,y,z} 3 f_{ik}(t) r_i r_k, \tag{2}$$

f_{ik} are linear combinations of F_{2m}. The algebra has proven to be more convenient with f_{ik}. Since a shear flow induces a shape deformation from a sphere which involves only second order harmonics (i.e., $n = 2$), as shown in [4], only $\mathcal{Y}_{2m}$ enter the calculation.

Our strategy is as follows [4,7,8]: The Stokes equations are solved for the velocity field inside and outside the vesicle subject to the membrane bending forces and to a fictitious force (actually a Lagrange multiplier) enforcing local membrane incompressibility. The integration constants of the velocity fields and the Lagrange multiplier are obtained by applying (i) the continuity of the (normal and tangential) velocity across the membrane, (ii) continuity of normal and tangential stress at the membrane, (iii) membrane incompressibility. A lengthy but straightforward algebra leads to a compatibility (or solvability) condition which results into the following evolution equation for the shape of the vesicle:

$$\frac{\mathcal{D} f_{ij}}{\mathcal{D} t} = \frac{20 e_{ij}}{23\lambda + 32} - \frac{192\pi}{23\lambda + 32} \frac{f_{xy} f_{ij}}{\Delta}, \tag{3}$$

where $e_{ij} = [\partial_i v_j + \partial_j v_i]/2$ is the symmetric part of the

velocity gradient of the unperturbed flow and $\lambda = \bar{\eta}/\eta$ is the viscosity ratio between the interior and the exterior, where Δ is the membrane excess area defined by $A = 4\pi + \Delta$, A being the dimensionless area of the vesicle.

The quantity $\mathcal{D}/\mathcal{D}t$ entering Eq. (3) is the Jaumann (or corotational) derivative defined as

$$\frac{\mathcal{D}\mathbf{M}}{\mathcal{D}t} = \frac{D\mathbf{M}}{Dt} + \frac{1}{2}[\omega\mathbf{M} - \mathbf{M}\omega], \tag{4}$$

where $\mathbf{M}$ is any second order tensor, D/Dt is the usual material derivative, and $\omega = (\nabla\mathbf{v} - \nabla\mathbf{v}^T)/2$ is the vorticity tensor.

Equation (3) constitutes a basis for the derivation of the constitutive law. The rheological relation is obtained by performing the spatial average of the stress over the total volume V [9,10]: $\langle\sigma_{ij}\rangle = \frac{1}{V}\int_V \sigma_{ij}dV$. After some manipulation it can be shown [9,10] that

$$\langle\sigma_{ij}\rangle = 2\eta e_{ij} + \frac{1}{V}\int_A [\sigma_{ik}x_j n_k - \eta(v_i n_j + v_j n_i)]dA.$$

The second part, which consists in integration over the vesicle area A, accounts for the vesicle contribution ($\mathbf{n}$ is the normal to the vesicle). This will result in an alteration of the fluid rheological properties.

Using the solution of the hydrodynamical problem as a function of the vesicle deformation [4] (as explained above), the average stress tensor is computed [11]. The result can be expressed in a compact form: $\langle\sigma_{ij}\rangle = \sigma^0_{ij} - 3\eta\phi T_{ij}$, where $\sigma^0_{ij} = 2\eta e_{ij}$ is the stress in the vesicle-free fluid and ϕ is the volume fraction of the suspension. $T_{ij}(t)$ enters the coefficients of the pressure field of the Lamb solution [4] and is the analogue of the shape perturbation amplitude f_{ij}. In particular, $T_{ij}(t)$ can be expressed in terms of amplitudes of spherical harmonics, as in (2). The boundary conditions (continuity of velocity and stresses) link together the unknown coefficients f_{ij}, T_{ij} (and others entering the Lamb solution [4,8]). Writing T_{ij} in terms of f_{ij} (see also [12]), we find

$$\frac{\sigma_{ij}}{2\eta} = e_{ij} + \phi\left(\frac{5}{2} - 2h\sqrt{\frac{15}{2\pi}}\right)e_{ij} + \phi h\sqrt{\frac{15\pi}{2}}\frac{96 f_{xy} f_{ij}}{5\Delta}, \tag{5}$$

where we have dropped the average symbol, and $h = 60\sqrt{2\pi/15}/(23\lambda + 32)$. Note that for a dilute polymer solution [13], when the polymer is represented by an elastic dumbbell, the so-called upper convected derivative, $D\mathbf{M}/Dt - [\nabla v\mathbf{M} + \mathbf{M}\nabla v^T]$, enters the rheological equation instead of the corotational derivative, obtained here. This can be traced back to the geometrical nature of the suspended entities (a quasisphere in the present case, and a dumbbell in the polymer case).

Equations (3) and (5) summarize the rheological equations of the composed fluid. In principle f_{ij} is determined from Eq. (3). Plugging the result into Eq. (5) determines the stress tensor. The equilibrium condition $\partial_i\sigma_{ij} = 0$ provides us with the closure relation. An important point is worth mentioning. For droplet [8] and capsule models [14] the shape evolution equation is, to leading order, apart from the Jaumann derivative, linear. This markedly contrasts with the present situation where the evolution equation is nonlinear due to local membrane incompressibility. The nonlinearity results in rich dynamics (as compared to droplets and capsules) where a tank-treading motion with a fixed orientation angle may lose stability in favor of tumbling via a saddle node bifurcation. In addition, a vacillating-breathing mode coexists with tumbling [4]. These dynamics strongly impact on the rheological properties, as seen below.

We determine now the rheological properties and set up a link between microscopic dynamics and rheology. In the tank-treading regime Eq. (3) can be solved analytically. We find a stationary solution given by

$$f_{xy} = \frac{1}{12h}\sqrt{\frac{15\Delta(4h^2 - \Delta)}{8\pi}}. \tag{6}$$

This solution exists provided that $4h^2 < \Delta$. In this regime the vesicle makes an angle [4] $\psi = \psi_0 = \pm\frac{1}{2}\cos^{-1}(\sqrt{\Delta}/2h)$ with the shear direction, while its membrane undergoes a tank-treading-like motion. Having determined f_{xy}, we are in a position to determine the effective viscosity by making use of Eq. (5). We find

$$\eta_{\text{eff}} = \eta\left[1 + \frac{5}{2}\phi - \phi\sqrt{\frac{15}{8\pi}}\frac{\Delta}{h}\right], \tag{7}$$

which extends the famous Einstein [15] result to the case of vesicles [4].

Let us now turn to the more general case of time-dependent dynamics. From the above rheological equations, it is easy to show that the full expression of the time-dependent effective viscosity η^D_{eff} is given by [defined by $\eta^D_{\text{eff}} = \sigma_{xy}/\dot{\gamma}$, with σ_{xy} given by (5)]

$$\frac{\eta^D_{\text{eff}}}{\eta} = 1 + \frac{5}{2}\phi\left(1 - \frac{4}{5}\sqrt{\frac{15}{2\pi}}h\right) + \frac{\phi}{\Delta}h\sqrt{\frac{470}{\pi}}R^2\sin^2(2\psi)$$

where we have expressed the shape function in terms of spherical harmonics by using the relation $F_{22} = \text{Re}^{-2i\psi}$, where ψ is the vesicle orientation angle in the flow, and R is the amplitude of deformation about the sphere [4].

The above expression of dynamical viscosity is valid for a single vesicle (see below). This computation is instructive from the conceptual point of view. As an example we show the orientation angle ψ and η^D_{eff} in the tumbling regime (Fig. 1). The viscosity shows a nontrivial dynamical behavior. It exhibits a minimum at $\psi = 0$, which is intuitive, as the vesicle aligns along the flow. Surprisingly, another minimum is found at $\psi = \pi/2$. To the understanding of the authors, this is due to the fact that at the same time the shape elongation is minimal at $\psi = \pi/2$.

To compute the normal stress differences $N_1 = \sigma_{xx} - \sigma_{yy}$ and $N_2 = \sigma_{yy} - \sigma_{zz}$ the determination of the diagonal

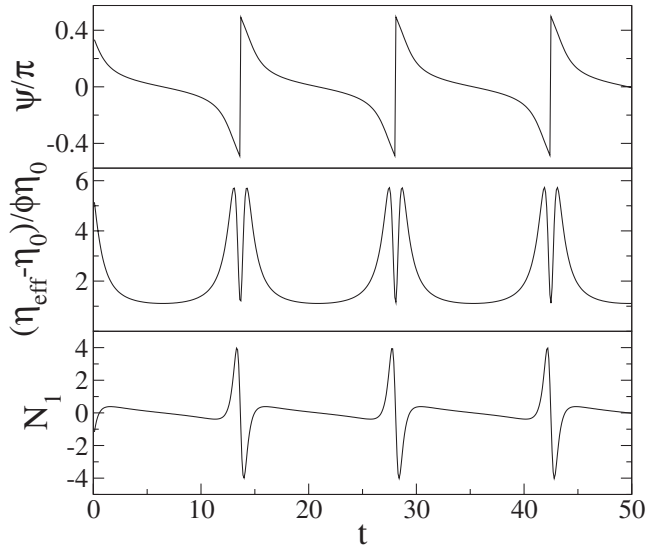

FIG. 1. The time-dependent orientation angle (upper panel), the time-dependent viscosity (middle panel) and the first normal stress difference (lower panel) in the tumbling regime.

elements of f_{ij} is required. We obtain from (3)

$$f_{xx} = -f_{yy} = \frac{\Delta}{48h}\sqrt{\frac{30}{\pi}}, \qquad f_{zz} = 0, \tag{8}$$

so that (here we switch to physical variables)

$$N_1 = -2N_2 = \eta\dot{\gamma}\phi\sqrt{\frac{15\Delta(4h^2-\Delta)}{2\pi h^2}}. \tag{9}$$

Here it is also seen that N_1 decreases with decreasing h (or equivalently increasing λ). This is valid in the tank-treading regime. In the time-dependent regime we can express $N_{1,2}$ in terms of R and ψ. A simple conversion of f_{ij} into F_{ij} yields from the full expression (5)

$$N_1^D = -2N_2^D = \frac{16\eta\dot{\gamma}\phi}{\Delta}\sqrt{\frac{15}{32\pi}}R^2\sin(4\psi). \tag{10}$$

Like the viscosity, N_1^D is a nonlinear time-dependent function of time, as shown in Fig. 1 (lower panel).

What happens to the rheological properties if the tumbling boundary in parameter space is crossed? While the tank-treading motion can be analyzed analytically down to the tumbling bifurcation, in the tumbling regime it has not been possible to obtain analytical expressions. We have thus solved Eq. (3) numerically. For definiteness we fix $\Delta = 1$, but the overall qualitative features do not depend on this choice. As shown above, in the last two regimes η_{eff}^D and $N_{1,2}^D$ are nonlinear oscillating functions of time. The instantaneous values of these quantities are of fundamental interest, since they provide the link between the orientation and the amplitude deformation and the actual rheological properties. From the practical point of view the average quantities over a period are of interest since a realistic suspension consists of individual vesicles with uncorrelated dynamics.

While the tumbling threshold is approached $\langle\eta_{\text{eff}}^D\rangle$ undergoes a decline. In the tumbling regime η_{eff} exhibits a sudden increase (Fig. 2). Recalling that the tumbling threshold corresponds to $h = \sqrt{\Delta}/2 \equiv h_c$, we find from (7) that for $h \simeq h_c$

$$\frac{\eta_{\text{eff}}}{\eta} \equiv 1 + \frac{5}{2}\phi\left(1 - \frac{2}{5}\sqrt{\frac{15\Delta}{2\pi}}\right) + \phi\sqrt{\frac{30}{\pi}}(h - h_c). \tag{11}$$

From the tumbling side it is seen from Fig. 2 (inset) that $\langle\eta_{\text{eff}}^D\rangle$ can be fitted with a linear function in terms of $h_c - h$. Combining this result and the above analytical one, we can conclude that the viscosity exhibits a cusp singularity, $\eta_{\text{eff}} \sim |\lambda - \lambda_c|$ at the critical viscosity contrast λ_c at which tumbling takes place. The same conclusion can be drawn regarding the VB mode. This singularity is believed to be a general feature, beyond the small deformation theory. It reflects the behavior of the fold catastrophe associated with the tumbling bifurcation. Note that the VB mode shows a smaller viscosity than the tumbling one. The tumbling regime possesses a higher viscosity than the tank-treading one at the same distance from the bifurcation point. Several remarks are in order. The sudden increase of $\langle\eta_{\text{eff}}^D\rangle$ in the tumbling regime can be traced back to the fact that over a period the vesicles scan a larger cross section against the flow than in the tank-treading regime and in the VB one. As one moves far into the tumbling regime the period of rotation becomes smaller and smaller as compared to $\dot{\gamma}^{-1}$, so that on the time scale of the imposed flow the flow capability is reduced further and further. The same reasoning holds for the VB mode.

Another important feature is obtained from the analysis of $\langle N_1^D\rangle$ and $\langle N_2^D\rangle$, as shown on Fig. 3. Both quantities

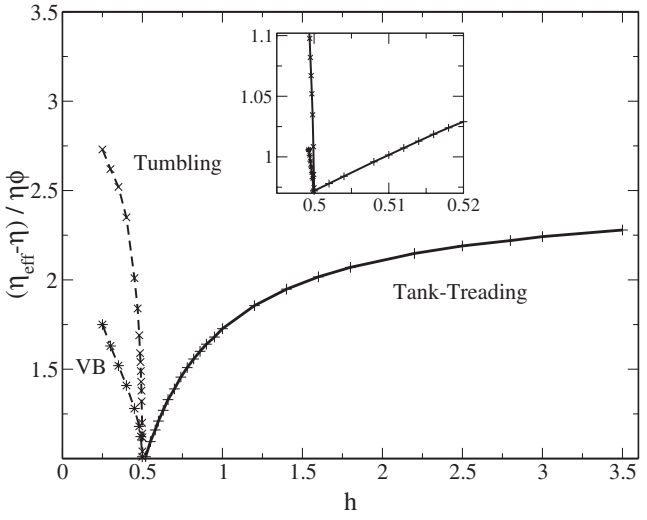

FIG. 2. The reduced average effective viscosity as a function of h for the various three regimes: tank-treading, tumbling, and vacillating-breathing (VB). The inset shows a cusp singularity at the tumbling bifurcation point.

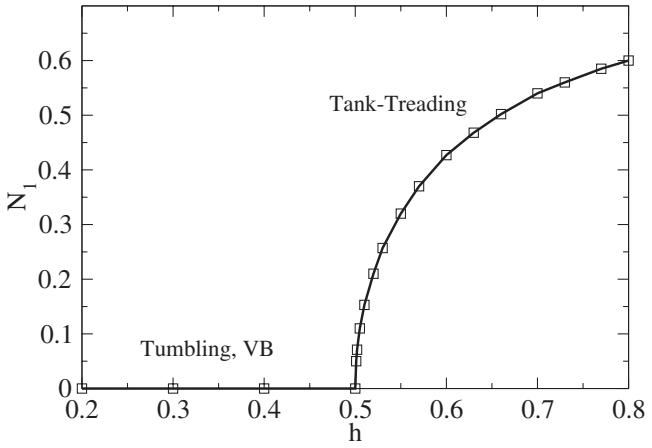

FIG. 3. The first normal stress difference N_1 as a function of h for the various three regimes: tank-treading, tumbling and vacillating-breathing (VB).

exhibit a collapse (in absolute values) towards a vanishing value at the bifurcation point. In the tumbling and VB regimes N_1 and N_2 remain very close (up to numerical accuracy) to a zero value. From the tank-treading side they exhibit a square root singularity, which is directly connected to the behavior of the orientation angle. Indeed from (9) it is simple to show that for $h \simeq h_c$

$$N_1 = -2N_2 = 2\eta\dot{\gamma}\phi\left(\frac{30}{\pi}\right)^{1/2}\Delta^{-1/4}(h - h_c)^{1/2}. \quad (12)$$

Normal stress differences are usually attributed to elongation of the suspended entities along the flow. Here, in the tumbling regime, there is on average no preferred orientation of the vesicle, so that the fluid behaves from this perspective as a Newtonian one.

Note that an experimental study of the rheological properties requires monodisperse samples by varying the viscosity contrast using dextran solutions (Mader *et al.* [6]). Obtaining monodisperse samples by observing the same excess area is a challenging task in general. Microfluidic devices [16] constitutes now a promising tool to achieve this goal.

Several issues deserve future considerations. First, fluctuations of the membrane must be taken into account. Similarly, an extension of the theory to higher deformation is needed for the sake of more systematic comparison with future experiments on rheology. We expect these two effects to lead to shear thinning, and to a variation of N_1 and N_2 with the shear rate. However, for a given shear rate, we expect the overall qualitative features reported in Fig. 1 and 2 unaffected. Second, it has been found here that the dynamics that prevails can not be explained by a reduction of the effective viscosity (for example the viscosity in the tumbling regime may be higher than that in the tank-treading one).

In summary, a rheological law has been derived that is distinct from that of droplet and capsule theories, owing to the membrane inextensibility. This results in a nonlinear rheological law and a nonlinear shape equation. The nonlinear shape equation triggers bifurcations, and coexistence of modes, conferring new qualitative features to the present system. We have set up a link between microscopic dynamics and rheology, and have shown that an analysis of the suspension at the global scale exhibits signatures of the microscale dynamics. These signatures are accessible experimentally, and we hope that this work will incite experimental research along this direction.

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