ISSN 0021-3640, JETP Letters, 2008, Vol. 87, No. 9, pp. 511–515. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © S.S. Vergeles, 2008, published in Pis'ma v Zhurnal Éksperimental'noĭ i Teoreticheskoĭ Fiziki, 2008, Vol. 87, No. 9, pp. 597–601.

Rheological Properties of a Vesicle Suspension

S. S. Vergeles

Landau Institute for Theoretical Physics, Russian Academy of Sciences, Chernogolovka, Moscow region, 142432 Russia

Received March 27, 2008

The rheological properties of a vesicle suspension have been investigated in the limit of strong flows destroying the stationary form of vesicles. The dependence of the effective viscosity of the suspension on the velocity gradient and the properties of vesicles has been obtained for the case of the plane flow. In particular, it has been shown that the effective viscosity of the suspension can strongly depend on its initial state. The effect of thermal fluctuations on the rheological properties of the suspension has been analyzed.

PACS numbers: 47.50.-d, 47.57.E-, 66.20.Cy

DOI: 10.1134/S0021364008090130

1. Investigation of the rheological properties of suspensions of microparticles is of great interest in view of their wide application in engineering and biology, where blood is the main example of suspensions. The suspension of the simplest particles—solid balls—was considered by Einstein [1]. More recently, the results of work [1] were generalized to the case where particles are drops of another liquid with a different viscosity in the limit of the strong surface tension [2]. The diluted vesicle suspension is considered in this work.

In contrast to a simple liquid drop, a vesicle consists of the liquids of the solvent and the drop separated by a membrane. Let us consider vesicles in which a membrane is a double layer of lipids and is in the liquid state. The properties of vesicles have been actively investigated in recent years. One of the causes of increased interest is that a vesicle is a simplified model of red corpuscles. Hence, the investigation of the mechanical properties of the vesicle can provide a key to the understanding of the mechanical properties of the red corpuscles. Another cause is the possible use of vesicles in pharmacology for the transport of medicines to diseased organs.

In contrast to solid balls and drops considered in [2], the vesicle undergoes deformations. As a result, the rheological properties of the vesicle suspension are more complex. As shown in this work, the effective viscosity η_s of the vesicle suspension depends on the flow geometry. Moreover, the viscosity of the suspension for some flow geometries depends on its initial state, because vesicles in such flows can be in different locally stable dynamic regimes. In particular, if an action transferring vesicles from one dynamic regime to another exists, this action would change the effective viscosity of the suspension.

The behavior of an individual vesicle in the external flow was theoretically studied in [3]. Vesicles with a viscosity contrast different from unity were experimentally investigated in [4, 5]. The first theoretical predictions for such an experiment were presented in [6, 7]. In those works, the effect of the bending forces of the membrane was disregarded; although these forces are relatively small, they are important and strongly change the phase diagram of the dynamic regimes of the vesicle. The effect of the bending forces of the membrane was first revealed by means of the numerical simulation [8] and was then consistently taken into account in [9, 10]. The rheological properties of the vesicle suspension were studied in [11]; however, that work was based on the incomplete results from [6].

The free energy of the incompressible closed membrane is written in the form of the surface integral [12, 13]

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

Here, $H = 1/R_1 + 1/R_2$ is the average curvature of the membrane surface, where R_1 and R_2 are the local curvature radii of the membrane. The first term in Eq. (1) is the energy associated with the deformation of the shape of the membrane. Expression (1) for the free energy does not include linear terms in H, because the membrane sides are considered as symmetric. The surface tension σ in Eq. (1) is determined from the requirement of the incompressibility of the surface flow of the membrane.

The diffusion of the liquid through the membrane is sufficiently slow; hence, the membrane in rheological experiments can be treated as impermeable for the liquid. Thus, the vesicle volume $\mathcal{V}$, as well as the total area $\mathcal{A}$ of the vesicle surface, is conserved. Let the size R of the vesicle be related to its volume as $4\pi R^3/3 = \mathcal{V}$. In this case, the area of the vesicle is given by the expression $\mathcal{A} = (4\pi + \Delta)R^2$. The nonnegative parameter Δ characterizes the deviation of the vesicle shape from a sphere for which this parameter is zero. Let us consider quasi-spherical vesicles characterized by the condition $\Delta \ll 1$.

It is convenient to specify the shape of the quasi-spherical vesicle in the spherical coordinates (r, ϑ, ϕ) by means of a dimensionless function of the spherical angles $u(\vartheta, \phi)$. The position of the vesicle surface element is specified by the equality $r = R(1 + u)$. The function amplitude is $u \sim \sqrt{\Delta}$. In the leading approximation with respect to the asphericity of the vesicle shape, the function u specifying the vesicle shape can be represented in the form of the second-order spherical harmonic

$$u = \frac{\sqrt{5\Delta}}{4\sqrt{2\pi}}\Big[\frac{\sin\Theta\cos J}{\sqrt{3}}(1 - 3\cos^2\theta) + \cos\Theta\sin^2\theta\cos(2\phi - 2\Phi) + 2\sin\Theta\sin J\cos(\phi - \Psi)\Big]. \quad (2)$$

This parameterization automatically ensures the conservation of the total area of the vesicle surface.

The boundary condition on the vesicle is the continuity of the velocity field in the entire space. All inertial effects are neglected owing to the smallness of the Reynolds number. For this reason, the force appearing on the membrane should be compensated for by the difference of the momentum fluxes in liquids on different sides of the membrane.

In this work, the case of the plane flow is considered as one of the most interesting cases for experiments. The coordinate system is chosen so that only the components $\partial_y v^x_{(0)} = s + \omega$ and $\partial_x v^y_{(0)} = s - \omega$ are nonzero in the gradient matrix of the velocity field $\mathbf{v}_{(0)}$ unperturbed by the vesicle.

According to [9, 10], the dynamic regime of the vesicle is determined by two parameters S and Λ, which are related to the physical parameters as

$$S = \frac{14\pi}{3\sqrt{3}}\frac{s\eta R^3}{\kappa\Delta}, \qquad \Lambda = \frac{2\sqrt{2}}{\sqrt{15\pi}}\frac{\sqrt{\Delta}\omega}{s}\Big(1 + \frac{23\tilde{\eta}}{32\eta} + \frac{\zeta}{2\eta R}\Big), \quad (3)$$

where η is the solvent viscosity, $\tilde{\eta}$ is the viscosity of the liquid inside the vesicle, and ζ is the surface viscosity of the membrane, which can be significant if the temperature is close to the temperature of the main transition of the membrane [14]. In the limit of strong external flows, $S \gg 1$ and the dynamic regime of the vesicle is specified only by the parameter Λ.

2. The effective instantaneous viscosity of the suspension is given by the expression

$$\eta_s = \eta W/W^{(0)}, \quad (4)$$

where the powers spent by the external forces W and $W^{(0)}$ in the flows of the suspension and pure liquid, respectively, are measured with the same boundary conditions for velocity (see, e.g., [15]). The flow occurs with low Reynolds numbers and, hence, is described by the Stokes equation. For this reason, the power W is expressed in the form

$$W = W^{(0)} + \sum_a W^a, \quad (5)$$

where the summation is performed over all suspended vesicles and W^a can be called power absorbed by an individual vesicle. The velocity of the solvent in the suspension is represented in the form $\mathbf{v} = \mathbf{v}_{(0)} + \delta\mathbf{v}$, where $\mathbf{v}_{(0)}$ is the flow velocity of the pure liquid. (The gradient of the unperturbed velocity field $\partial_j v^i_{(0)}$ is assumed to be constant in space.) Let us consider an individual vesicle and define the spherical coordinate system introduced above. The term W^a in Eq. (5) referring to the vesicle under consideration can be represented in the form of the integral over the $r = R$ sphere,

$$W^a = -\frac{5\eta\mathcal{V}}{2}\int\frac{do}{4\pi}3h\Big[\frac{4\delta v^r}{R} + \partial_r\delta v^r\Big]\Big|_{r=R}, \quad (6)$$

where do is the solid angle element, $h = \partial_j v^i_{(0)} n^i n^j$, and $\mathbf{n} = \mathbf{r}/r$ is the unit vector. Expression (6) is written under the assumption that the vesicle volume is constant. The velocity field value $\delta\mathbf{v}$ on the $r = R$ sphere is obtained by its analytic continuation from the region filled with the solvent.

The diluted suspension limit is considered; in this case, the volume fraction φ occupied by suspended particles is small, $\varphi \ll 1$. In the diluted limit, it can be assumed that each suspended particle is in the unperturbed velocity field $\mathbf{v}_{(0)}$, whereas the perturbed part of the velocity field $\delta\mathbf{v}$ near a vesicle is created only by this vesicle.

The dynamics of the vesicle shape in the external flow was determined in [9, 10]. To find δv^r and $\partial_r\delta v^r$ in Eq. (6), the boundary conditions on the vesicle surface should be related to the boundary conditions on the surface of the sphere of the radius R. This relation is significantly nonlinear and is generally written in the integral form (see, e.g., [16]). For the case of the quasi-spherical vesicle, these equations can be simplified by expanding them in the small parameter $\sqrt{\Delta}$ up to the first order. In this expansion, it should be taken into account that the functions u and $\dot{u}$ have generally the first and zeroth orders in $\sqrt{\Delta}$, respectively [10]. As a result,

$$\begin{aligned} \delta v^r/R &= -h + \dot{u} + u\dot{u} - \omega\partial_\phi u/\sin^2\theta, \\ \partial_r \delta v^r &= -h + 5u\dot{u} - (15/2)hu. \end{aligned} \tag{7}$$

On the both sides of Eqs. (7), the projection on the second-order spherical harmonic is implied, because it only makes a nonzero contribution to integral (6). The terms $-h$ corresponding to the rigid sphere of the radius R are separated on the right-hand side of Eqs. (7).

3. To calculate the time-averaged effective viscosity of the suspension, Eqs. (7) should be averaged over the vesicles and time. After that, the complete time derivatives disappear and only the first and last terms are significant in Eqs. (7). The dimensionless deviation of effective viscosity (4) from its value for the pure liquid is

$$\frac{\eta_s - \eta}{\varphi\eta} = \frac{5}{2} + \langle\sqrt{\Delta}Q\rangle_{\text{vesicles}}. \tag{8}$$

A term of 5/2 corresponding to the contribution to the viscosity of rigid spheres with the radius R is separated on the right-hand side of Eq. (8). The angular brackets mean averaging over all vesicles. For the plane flow, the quantity Q for one vesicle is determined by the expression

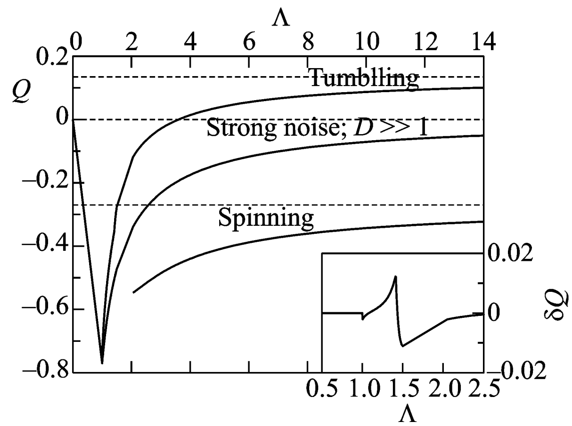
$$Q = \frac{5\sqrt{15}}{8\pi}\left\langle\frac{\sqrt{6}}{7}\sin\Theta\cos J - \frac{\omega}{s}\cos\Theta\cos(2\Phi)\right\rangle_{\text{time}} \tag{9}$$

and is generally about unity. The angular brackets in Eq. (9) denote the time averaging.

When $\Lambda < \sqrt{2}$, the vesicle is in the tank-treading regime in which the shape and orientation of the vesicle found in [10] remain unchanged. Time averaging in Eq. (9) is reduced to the exclusion of the relaxation of the vesicle shape to the stationary state and provides

$$Q = \frac{5\sqrt{15}}{8\pi}\begin{cases} -(\omega/s)\Lambda, & 0 < \Lambda < 1 \\ \frac{\sqrt{6}}{7}\sqrt{1 - \frac{1}{\Lambda^2}} - \frac{\omega}{s\Lambda}, & 1 < \Lambda < \sqrt{2}. \end{cases} \tag{10}$$

When $\Lambda > \sqrt{2}$, the vesicle is in the trembling regime, which is transformed to the tumbling regime with a further increase in Λ. In these regimes, both the shape and orientation of the vesicle undergo periodic oscillations. For this reason, time averaging in Eq. (9) becomes significant. In order to perform this averaging, the equations of motion for the vesicle shape, which were obtained in [10], should be used. The result is rather lengthy and is not presented here. Note only that Q at $\Lambda \gg 1$ tends to ≈ 0.13. The $Q(\Lambda)$ plot is shown in the figure.



Quantity Q versus parameter Λ for various dynamic regimes and its value in the limit $\mathfrak{D} \gg 1$. The inset is the correction δQ versus Λ for the tank-treading, trembling, and tumbling regimes for $\mathfrak{D} = 0.01$.

When $\Lambda > \sqrt{3}$, the vesicle can also be in the spinning process. The choice between the tumbling and spinning regimes depends on the initial state of the vesicle. In the spinning regime,

$$Q = -\frac{5\sqrt{15}}{8\pi\Lambda}\left(\frac{\sqrt{3(2\Lambda^2 - 5)}}{7} + \frac{\omega}{s}\right), \tag{11}$$

where the parameters of the motion of vesicles in the spinning regime that were found in [10] were used.

4. The effects of the thermal fluctuations on the vesicle dynamics are strongly different for the regions $\Lambda < 1$ and $\Lambda > 1$. When $\Lambda < 1$, the vesicle is in the tank-treading state, and the relaxation time for the vesicle shape to the stationary shape is determined by the external flow strength. The intensity of the thermal fluctuations is determined by the ratio $T/\Delta^2\kappa S$, which is small for $S \gg 1$. For this reason, when $\Lambda < 1$, the contribution of thermal fluctuations to the vesicle suspension viscosity can be neglected.

As shown in [10], the properties of the vesicle dynamics for $\Lambda > 1$ are strongly different. The external flow initiates the motion of the phase-space point $\{\Theta, \Phi, J, \Psi\}$ in Eq. (2) over the closed trajectories. Two independent slow variables remain constant in this motion. These slow variables vary in time due to the bending forces determined by the modulus κ in Eq. (1). In view of this circumstance, the relaxation of slow variables to their stationary values occurs at times much longer than the characteristic time of vesicle oscillations induced by the external flow. For this reason, the role of the thermal fluctuations responsible for the oscillations of slow variables increases significantly at $\Lambda > 1$ and is determined by the dimensionless parameter $\mathcal{D} = T/\kappa\Delta^{3/2}$.

Let us first consider the limit $\mathcal{D} \gg 1$. In this limit, thermal fluctuations are so strong that they destroy the equilibrium shape of the vesicle in the absence of the external flow. In this case, the effect of the bending forces on the vesicle molecules can be neglected. To obtain the average value of the quantity Q given by Eq. (9), it is necessary to average first through the trajectories with constant values of slow variables and, then, over the distribution function in the slow-variable space, which is due to the thermal fluctuations. The result of this procedure, which can be completed only numerically, is shown in the figure.

In the opposite limit, $\mathcal{D} \ll 1$, the $Q(\Lambda)$ curves corresponding to the tumbling and spinning regimes are slightly perturbed. The difference $\delta Q = Q(\Lambda, \mathcal{D}) - Q(\Lambda, 0)$ of the Q values in the presence and absence of noise is of interest.

The $\delta Q(\Lambda)$ curve for the tumbling regime that is shown in the inset has a singularity near the transition from the tank-treading regime to the trembling regime at $\Lambda = \sqrt{2}$ and near the point $\Lambda = 1$. After the expansion near the point $\Lambda = \sqrt{2}$, the distribution function of the nonnegative quantity $q = Q(\Lambda, \mathcal{D}) - Q(\sqrt{2}, 0) - 0.52\delta\Lambda$ has the form

$$\mathcal{P} \propto \exp\left\{-\frac{(q-(0.71\delta\Lambda - 2.5\mathcal{D}))^2}{0.089\mathcal{D}}\right\}, \qquad (12)$$

where $\delta\Lambda = \Lambda - \sqrt{2}$. Distribution function (12) has the singularity shown in the inset. When Λ is close to one, i.e., $\Lambda - 1 = \delta\Lambda \ll 1$, the main contribution to the thermal correction of viscosity comes from thermal fluctuations of the parameter J, which are determined by the average $\langle J^2\rangle = \mathcal{D}\sqrt{2/\delta\Lambda}$ (this equality is valid at $\delta\Lambda \gg \mathcal{D}^2$). In view of this feature, the correction to the viscosity, δQ, approaches a negative value of about $-0.27\mathcal{D}$ at $\delta\Lambda \longrightarrow 0$. Finally, the correction δQ approaches a positive value of about $0.02\mathcal{D}$ in the limit of large values $\Lambda \gg 1$.

In the spinning regime at large viscosity contrasts, when $\Lambda \longrightarrow \infty$, the thermal correction δQ is more sensitive to thermal noise compared to the tumbling regime, $\delta Q \approx 0.2\sqrt{\mathcal{D}}$. At $\Lambda \longrightarrow \sqrt{3}$, the thermal correction approaches the value $\delta Q \approx 1.3\mathcal{D}$. The transition from the spinning regime to the tumbling regime at $\Lambda = \sqrt{3}$ proceeds through a saddle point. Thermal fluctuations accelerate this transition so that the spinning regime becomes unstable at $\Lambda - \sqrt{3} \lesssim \mathcal{D}^{2/3}$.

5. The vesicle is a deformable body. In this work, it has been shown that this fact leads to the dependence of the effective viscosity of the suspension given by Eq. (4) on the flow geometry. In the limit of strong plane flows, where $S \gg 1$, this dependence is observed for the region $\Lambda \lesssim 1$. According to Eq. (8), the relative amplitude of oscillations of the effective viscosity η_s that are due to the dependence of the matrix elements of the velocity field on the ratio ω/s is about $\sqrt{\Delta}$. The dependence of the effective viscosity of the suspension η_s on the geometry of the velocity field disappears at $\Lambda \gg 1$: the time-averaged second term in Eq. (9) (without the factor ω/s) is proportional to $1/\Lambda$ for all three curves in the figure, whereas the averaged first term in the leading approximation is independent of Λ.

In the region $\Lambda > \sqrt{3}$, there is another qualitative effect: the suspension viscosity depends on the initial state of the suspension and can be changed by means of the external action on the vesicles. In the tumbling regime, the vesicles have a symmetry under the reflection with respect to the flow plane (in the introduced coordinates, this means the change $z \longrightarrow -z$). In the spinning regime, this symmetry is absent, and the angle between the principal axis of the vesicle and the z axis is acute. The external action transferring the vesicles from one regime to another would change the effective viscosity of the suspension. According to the above consideration, such an external action should be reduced to the assignment or violation of the symmetry under the $z \longrightarrow -z$ transformation.

New qualitative effects can appear in an unsteady flow of the vesicle suspension. These effects can be studied in subsequent investigations. Note that Eqs. (7) can be used to calculate the suspension viscosity at finite frequencies.

I am grateful to V.V. Lebedev for discussions and valuable advices. This work was supported in part by the Russian Foundation for Basic Research (project nos. 06-02-17408-a and 06-02-72028, the latter jointly with the Ministry of Science and Technology of Israel), by the Russian Science Support Foundation, and by the Council of the President of the Russian Federation for Support of Young Scientists and Leading Scientific Schools (project no. NSh-4930.2008.2).

REFERENCES

1. A. Einstein, Ann. Physik. **34**, 592 (1911).
2. G. I. Taylor, Proc. Roy. Soc. A **138**, 41 (1932).
3. U. Seifert, Eur. Phys. J. B **8**, 405 (1999).
4. Kantsler and V. Steinberg, Phys. Rev. Lett. **95**, 258101 (2005).

5. V. Kantsler and V. Steinberg, Phys. Rev. Lett. **96**, 036001 (2006).
6. C. Misbah, Phys. Rev. Lett. **96**, 028104 (2006).
7. P. M. Vlahovska and R. S. Gracia, Phys. Rev. E **75**, 016313 (2007).
8. H. Noguchi and G. Gompper, Phys. Rev. Lett. **98**, 128103 (2007).
9. V. V. Lebedev, K. S. Turitsyn, and S. S. Vergeles, Phys. Rev. Lett. **100**, 028103 (2008).
10. V. V. Lebedev, K. S. Turitsyn, and S. S. Vergeles, New J. Phys. (in press); arXiv:0705.3543.
11. G. Danker and C. Misbah, Phys. Rev. Lett. **98**, 088104 (2007).
12. W. Helfrich, Z. Naturforsch. B **103**, 67 (1975).
13. E. I. Kats, V. V. Lebedev, and A. R. Muratov, JETP Lett. **63**, 217 (1996).
14. R. Dimova, B. Pouligny, and C. Dietrich, Biophys. J. **79**, 340 (2000).
15. J. Happel and H. Brenner, *Low Reynolds Number Hydrodynamics* (Prentice-Hall, Englewood Cliffs, 1965; Mir, Moscow, 1976).
16. O. A. Ladyzhenskaya, *The Mathematical Theory of Viscous Incompressible Flow* (Gordon and Breach, New York, 1987).

Translated by R. Tyapaev