



Drop deformation with soluble surfactants in linear flows: role of adsorption-desorption

Paul Regazzi, Marc Leonetti

► To cite this version:

Paul Regazzi, Marc Leonetti. Drop deformation with soluble surfactants in linear flows: role of adsorption-desorption. 2024. <hal-04750636>

HAL Id: hal-04750636

<https://hal.science/hal-04750636v1>

Preprint submitted on 23 Oct 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



HAL Authorization

Drop deformation with soluble surfactants in linear flows: role of adsorption-desorption

P. Regazzi* and M. Leonetti†

Aix Marseille Univ, CNRS, CINaM, Marseille, France.

October 22, 2024

Abstract

Drop deformation in shear flow is determined up to second order theory in Ca while considering kinetic effects on surfactants distributions in steady state. Surfactants inside the drop are adsorbed faster than those on the surface leading to an increase in total surfactants concentration on the semi-minor axis of the ellipsoidal droplet. New expressions for Taylor deformation and angle deviation are proposed involving kinetics effects. Theoretical calculations lead to a possibility of lesser deformation than the usual limit condition and a minor correction for the deviation angle.

1 Introduction

Rheology of fluids was first introduced by a work from Taylor (1932) that sought to study pure water drop deformation and breakup. It brought significant results in that field especially by quantitatively defining the difference between the main axis L and the smaller one S being $D_T = \frac{L-S}{L+S}$. A generalization in non stationary state was given by Cox (1969) which takes into account mechanical stress applied on the drop surface and describes its long-term equilibrium regime in shear flow and hyperbolic flow. Deformation and breakup of drops in dilute emulsion expressions were determined by Frankel and Acrivos (1970) and Barthes-Biesel and Acrivos (1973).

*Email address for correspondence: paul.regazzi@univ-amu.fr

†Email address for correspondence: marc.leonetti@univ-amu.fr

Later on, applications on more complex drops involving surfactants concentration evolution such as foam or red blood cells were investigated. Movements of surfactants inside and at the membrane of the drop counterbalance the surface tension, maximizing the deformation: this is the so-called Marangoni effect. It was widely explained by Stone and Leal (1990) and experimentally observed in Stone (1994) who considered advective-diffusive effects of surfactants in non-stationary flows and led to an increase of the Taylor deformation.

Another effect on surfactant-free droplets was first introduced by Flumerfelt (1980) and widely studied by Narsimhan (2019) involving surface viscosity effects when dealing with soluble surfactants hence increasing or decreasing Taylor deformation according to the range of values of the Boussinesq numbers $Bq_{\mu,\kappa}$.

Subsequently, rheology of fluids applied to other objects such as capsules and vesicles has proven to be worth the detour in the soft matter domain with experimental studies (tumbling and tank-treading in works from Dupire et al. (2012), Kaoui et al. (2009)), theoretical studies given by Keller and Skalak (1982)) and numerical studies by Gounley et al. (2016). However, the physics of surfactants' distribution and motion involved in such objects and droplets is much more complicated to observe and describe.

Surfactants are known to provide a significant contribution to the surface tension and tend to influence the ambient flow. A work from Vlahovska et al. (2009) considered the convective effect of surfactants at the surface of the drop and shew that it tends to counterbalance the viscosity in the Taylor deformation and even cancel the viscosity contribution at first order perturbation theory.

All these effects contributed to the Taylor deformation. However it seems that no matter the hypothesis made on the values for these quantities, D_T is determined by the conditions at infinity of the considered flow and isn't diminished by the aforementioned effects. Questions arise such as which phenomena could cause a lower D_T value than what is the usual result.

In this paper, following the work of Wailliez et al. (2024), we consider kinetic effects on surfactants; the drop contains surfactants inside moving towards the interface and the ones at the surface can move towards the center. Effects of desorption and adsorption will be thus considered in order to check if it could contribute to a lower Taylor deformation in shear flow. Section 2 gives a global overview of the problem using tensor calculus. Section 3 highlights expressions for Taylor deformation and angle deviation of the drop. The results are then discussed in section 4.

2 Problem statement

Consider a spherical droplet of radius R containing a fluid of viscosity η^* and soluble surfactants. The drop is immersed in another fluid of viscosity η . The mechanical equilibrium of strengths applied on the drop will lead to the drop deformation. Surfactants inside the droplet are considered to be free as they can be adsorbed or desorbed from the interface. From now on, implicit summation over repeated indices is taken as convention. Let (x_1, x_2, x_3) be Cartesian coordinates centered on the droplet.

2.1 Main equations

The radius of the droplet being at the order of the micrometer in experiments, the Reynolds number in the Navier-Stokes equation is small $Re \ll 1$. Consequently, the fluids' motion is well-described by the Stokes equation:

$$\begin{aligned} \partial_j^2 v_i &= \frac{1}{\eta} \partial_i P, & \partial_i v_i &= 0 \\ \partial_j^2 v_i^* &= \frac{1}{\eta^*} \partial_i P, & \partial_i v_i^* &= 0 \end{aligned} \quad (1)$$

where the superscript $*$ denotes all the quantities inside the droplet, $\partial_j = \partial/\partial x_j$ and P is the pressure. The undisturbed velocity speed is

$$v_i^\infty = \dot{\epsilon} (E_{ij} + \Omega_{ij}) x_j \text{ for } r = \sqrt{x_a x_a} \rightarrow \infty \quad (2)$$

E_{ij} is the symmetric rate-of-strain tensor, Ω_{ij} is the antisymmetric vorticity tensor and $\dot{\epsilon}$ is the shear rate. This paper will be focused on steady state solutions obtained by continuity at the interface at a distance R from the center of the drop. The main equations are velocity continuity and mechanical equilibrium

$$v_i - v_i^* = 0 \text{ for } r = R \quad (3)$$

$$(\eta \Pi_{ij} - \eta^* \Pi_{ij}^*) n_j = F_i \text{ for } r = R \quad (4)$$

where Π_{ij} is the hydrodynamical stress tensor, n_j is normal to the interface and F_i are the interfacial forces given by

$$F_i = -\gamma P_{jk} \partial_k P_{ij} - P_{ij} \partial_j \gamma + P_{jk} \partial_k \Sigma_{ij}^* \text{ for } r = R \quad (5)$$

The first term on the right hand-side is the stress due to the drop's curvature and comes from a paper submitted by Taylor (1932). The second term is the Marangoni stress proposed by a work from Stone and Leal (1990). And the third term (see Narsimhan (2019)) comes from the surface viscosity η_μ and dilational viscosity η_κ effect on total stress. Boussinesq numbers are deduced $Bq_{\kappa,\mu} = \eta_{\kappa,\mu}/\eta R$. Hence

$$\Sigma_{ij}^* = (-Bq_\kappa + Bq_\mu) P_{ij} P_{lm} \partial_m v_l^* - Bq_\mu P_{ik} (P_{kl} \partial_l v_n^* + P_{nl} \partial_l v_k^*) P_{nj} \quad (6)$$

2.2 Evolution equations

When submitted to the far-field flow, we assume that the flow lines will be deformed along the drop. As such the steady state evolution equation for the deformation is

$$v_i n_i = v_i^* n_i = 0 \text{ for } r = R \quad (7)$$

For surfactants concentration inside the drop, the flux vector is

$$j_i = -D \partial_i C + C v_i^*, \quad j_i n_i = -K_1 C \left(1 - \frac{\Gamma}{\Gamma_\infty}\right) + K_2 \Gamma \quad (8)$$

D is the diffusion coefficient inside the drop, K_1 is the kinetic adsorption coefficient and K_2 the kinetic desorption coefficient. Γ_∞ is the saturated surfactant concentration at the interface. Thus one also obtain the equation

$$v_i^* \partial_i C - D \partial_i^2 C = 0 \quad (9)$$

Solving such an equation implies a harmonic decomposition for C . The evolution equation becomes, much alike in Stone and Leal (1990),

$$P_{ij} \partial_j \left[P_{ik} \Gamma v_k^* - \hat{D} P_{kl} \partial_l \Gamma \right] + \Gamma (P_{ij} \partial_j n_i) (v_k^* n_k) = K_1 C \left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - K_2 \Gamma \quad (10)$$

with \hat{D} the diffusion coefficient at the interface.

2.3 Small-deformation analysis

We suppose the drop shape will be slightly deformed. As the capillary number arises in such a way that $Ca = \eta \dot{\epsilon} R / \bar{\gamma} \ll 1$ since experimental drops have small radii, it is quite natural to consider that all the quantities involved in the equations, especially the drop deformation quantity tensor $f\left(\frac{x_1}{r}, \frac{x_2}{r}, \frac{x_3}{r}\right)$ can be expanded in Ca . For instance

$$R = 1 + Ca f^{(1)} + Ca^2 \left[-A f^{(1)} f^{(1)} + f^{(2)} \right] + O(Ca^3) \quad (11)$$

$$\frac{\Gamma}{\bar{\Gamma}} = 1 + \Gamma' = 1 + Ca g^{(1)} + Ca^2 g^{(2)} + O(Ca^3) \quad (12)$$

$$\frac{C}{\bar{C}} = 1 + Ca h^{(1)} + Ca^2 h^{(2)} + O(Ca^3) \quad (13)$$

with A a constant determined using the volume conservation of the drop and the bar denoting the quantity at equilibrium. The normal vector also becomes

$$n_i = \frac{x_i}{r} - Ca \partial_i f^{(1)} + o(Ca^2) \quad (14)$$

Using the same method as in a work from Stone and Leal (1990) the surface tension is influenced by the following state equation

$$\hat{\gamma} = \gamma_0 + \hat{E} \ln(1 - \psi), \quad \psi = \frac{\Gamma}{\Gamma_\infty} \quad (15)$$

where γ_0 is the surface tension without surfactants, $\hat{\gamma}$ the surface tension at the interface and \hat{E} the Gibbs elasticity. In the linear regime the equation becomes

$$\hat{\gamma} = \gamma_0 - \hat{E}\psi \quad (16)$$

and the equilibrium state is

$$\bar{\gamma} = \gamma_0 - \hat{E}\bar{\psi}, \quad \bar{\psi} = \frac{\bar{\Gamma}}{\Gamma_\infty} \quad (17)$$

Using such a result and multiplying equation (4) by $1/\eta\dot{\epsilon}R$ the mechanical equilibrium equation becomes

$$(\Pi_{ij} - \lambda\Pi_{ij}^*) n_j = -\frac{1 - \hat{E}\bar{\psi}\Gamma}{Ca\bar{\gamma}} P_{jk}\partial_k P_{ij} + \frac{\hat{E}\bar{\psi}}{Ca\bar{\gamma}} P_{ij}\partial_j \Gamma' + P_{jk}\partial_k \Sigma_{ij}^* \quad (18)$$

with $\lambda = \eta^*/\eta$ the viscosity contrast. To recover Stone and Leal (1990) notations, one has

$$\beta = \frac{\hat{E}}{\gamma_0} \bar{\psi} \quad (19)$$

By defining the following non dimensional quantities

$$\zeta = \frac{\bar{\gamma}R}{\eta\bar{D}}, \quad k_1^* = K_1 \frac{R}{\bar{D}}, \quad k_2^* = K_2 \frac{R}{\bar{D}}, \quad \alpha = R \frac{\bar{C}}{\bar{\Gamma}} \quad (20)$$

The flux equations (8) and the evolution equation (10) writes

$$j_i = -\frac{D}{\bar{D}} \alpha \partial_i \frac{C}{\bar{C}} + Ca\zeta \alpha \frac{C}{\bar{C}} v_i^*, \quad j_i n_i = -k_1^* \alpha \frac{C}{\bar{C}} (1 - \psi) + k_2^* \frac{\Gamma}{\bar{\Gamma}} \quad (21)$$

The evolution equation for dimensionless surfactants is

$$P_{ij}\partial_j \left[Ca\zeta P_{ik} \frac{\Gamma}{\bar{\Gamma}} v_k^* - P_{il}\partial_l \frac{\Gamma}{\bar{\Gamma}} \right] + Ca\zeta \frac{\Gamma}{\bar{\Gamma}} (P_{ij}\partial_j n_i) (v_k^* n_k) = k_1^* \frac{C}{\bar{C}} (1 - \psi) - k_2^* \frac{\Gamma}{\bar{\Gamma}} \quad (22)$$

3 Solutions

Since we are dealing with the Stokes equations in a spherical drop, we introduce solid harmonics. The tensors used will require to be symmetrical and traceless in order to satisfy the Laplace equation and allow the solid harmonics decomposition

3.1 First order

To determine the expression of the velocities, we'll use one main result from Lamb (1924)

$$v_i = \varepsilon_{ijk} \partial_j (\chi x_k) + \partial_i \phi + \frac{n+3}{2(n+1)(2n+3)} r^2 \partial_i P - \frac{n}{(n+1)(2n+3)} P x_i \quad (23)$$

With n the solid harmonic's order. As shown by Cox (1969), the first harmonics that appear in the aforementioned flows are solid harmonics of degree 2. Using the same decomposition as in the work from Frankel (1968) we define

$$\begin{aligned} P^{(1)} &= T_{lm}^{(1)} \partial_l \partial_m r^{-1}, & \phi^{(1)} &= S_{lm}^{(1)} \partial_l \partial_m r^{-1}, & \chi^{(1)} &= C_l^{(1)} \partial_l r^{-1} \\ P^{*,(1)} &= T_{lm}^{*,(1)} r^5 \partial_l \partial_m r^{-1}, & \phi^{*,(1)} &= S_{lm}^{*,(1)} r^5 \partial_l \partial_m r^{-1}, & \chi^{*,(1)} &= C_l^{*,(1)} r^3 \partial_l r^{-1} \\ f^{(1)} &= F_{lm}^{(1)} r^5 \partial_l \partial_m r^{-1}, & g^{(1)} &= G_{lm}^{(1)} r^5 \partial_l \partial_m r^{-1}, & h^{(1)} &= H_{lm}^{(1)} r^3 \partial_l \partial_m r^{-1} \end{aligned} \quad (24)$$

To simplify the equations, we set $r = 1$. Such decompositions give the following quantities

$$v_i^{(1)} = 6S_{ji}^{(1)} x_j - 15S_{lm}^{(1)} x_m x_l x_i r^{-7} + \frac{3}{2} T_{lm}^{(1)} x_l x_m x_i - \varepsilon_{ijk} C_j^{(1)} x_k + 3\varepsilon_{ijk} C_l^{(1)} x_l x_k x_j \quad (25)$$

$$v_i^{*,(1)} = 6S_{ji}^{*,(1)} x_j + \frac{5}{7} T_{ji}^{*,(1)} x_j - \frac{2}{7} T_{lm}^{*,(1)} x_l x_m x_i - \varepsilon_{ijk} C_j^{*,(1)} x_k \quad (26)$$

$$\begin{aligned} \Pi_{ij}^{(1)} &= 3T_{lj}^{(1)} x_l x_i + 3T_{li}^{(1)} x_l x_j + 12S_{ij}^{(1)} - 60S_{li}^{(1)} x_l x_j - 60S_{lj}^{(1)} x_l x_i \\ &\quad - 30S_{lm}^{(1)} x_l x_m \delta_{ij} + 210S_{lm}^{(1)} x_l x_m x_i x_j - 15T_{lm}^{(1)} x_l x_m x_i x_j \end{aligned} \quad (27)$$

$$\Pi_{ij}^{*,(1)} = -\frac{25}{7} T_{lm}^{*,(1)} x_l x_m \delta_{ij} + 12S_{ij}^{*,(1)} + \frac{10}{7} T_{ij}^{*,(1)} + \frac{6}{7} T_{li}^{*,(1)} x_l x_j + \frac{6}{7} T_{lj}^{*,(1)} x_l x_i \quad (28)$$

$$\begin{aligned} \Sigma_{ij}^{(1)} &= Bq_\kappa \left[\left(6S_{lm}^{*,(1)} + \frac{9}{7} T_{lm}^{*,(1)} \right) \delta_{ij} x_l x_m + \left(-6S_{lm}^{*,(1)} - \frac{9}{7} T_{lm}^{*,(1)} \right) x_l x_m x_i x_j \right] \\ &\quad + Bq_\mu \left[-12S_{ij}^{*,(1)} - \frac{10}{7} T_{ij}^{*,(1)} + \left(12S_{lj}^{*,(1)} + \frac{10}{7} T_{lj}^{*,(1)} \right) x_l x_i \right. \\ &\quad + \left(12S_{li}^{*,(1)} + \frac{10}{7} T_{li}^{*,(1)} \right) x_l x_j + \left(-6S_{lm}^{*,(1)} - \frac{5}{7} T_{lm}^{*,(1)} \right) x_l x_m \delta_{ij} \\ &\quad \left. + \left(-6S_{lm}^{*,(1)} - \frac{5}{7} T_{lm}^{*,(1)} \right) x_l x_m x_i x_j \right] \end{aligned} \quad (29)$$

By using the continuity equations one obtains

$$\frac{1}{5} T_{ij}^{(1)} - 2S_{ij}^{*,(1)} - \frac{1}{5} T_{ij}^{*,(1)} + \frac{E_{ij}}{3} = 0 \quad (30)$$

$$\varepsilon_{ijk} C_k^{(1)} - \varepsilon_{ijk} C_k^{*,(1)} + \Omega_{ij} = 0 \quad (31)$$

$$\begin{aligned} & -\frac{3}{5} T_{ij}^{(1)} - \lambda \left(4S_{ij}^{*,(1)} + \frac{2}{5} T_{ij}^{*,(1)} \right) + \frac{2}{3} E_{ij} + (Bq_\kappa - Bq_\mu) \left(-\frac{6}{35} T_{ij}^{*,(1)} - \frac{4}{5} S_{ij}^{*,(1)} \right) \\ & + Bq_\mu \left(-\frac{26}{35} T_{ij}^{*,(1)} - \frac{28}{5} S_{ij}^{*,(1)} \right) = \frac{8}{5} F_{ij}^{(1)} + \frac{2}{5} \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} G_{ij}^{(1)} \end{aligned} \quad (32)$$

$$-9S_{ij}^{(1)} + \frac{3}{2} T_{ij}^{(1)} - 6S_{ij}^{*,(1)} - \frac{3}{7} T_{ij}^{*,(1)} + E_{ij} = 0 \quad (33)$$

$$-3\varepsilon_{ijk}C_k^{(1)} = 0 \quad (34)$$

$$\begin{aligned} & 72S_{ij}^{(1)} - 9T_{ij}^{(1)} - \lambda \left(12S_{ij}^{*,(1)} - \frac{3}{7}T_{ij}^{*,(1)} \right) + 2e_{ij} + (Bq_\kappa - Bq_\mu) \left(\frac{18}{7}T_{ij}^{*,(1)} + 12S_{ij}^{*,(1)} \right) \\ & + Bq_\mu \left(\frac{18}{7}T_{ij}^{*,(1)} + 12S_{ij}^{*,(1)} \right) = 12F_{ij}^{(1)} - 6\frac{\hat{E}\bar{\psi}}{\bar{\gamma}}G_{ij}^{(1)} \end{aligned} \quad (35)$$

where the well-know angular integral relations on the sphere

$$\int x_i x_j d\Omega = \frac{4\pi}{3}\delta_{ij}, \quad \int x_i x_j x_l x_m d\Omega = \frac{4\pi}{15}(\delta_{ij}\delta_{lm} + \delta_{il}\delta_{jm} + \delta_{im}\delta_{jl}) \quad (36)$$

$$\int x_i x_j x_l x_m x_p x_q d\Omega = \frac{4\pi}{105}(\delta_{ij}\delta_{lm}\delta_{pq} + 14 \text{ permutations}) \quad (37)$$

were used.

Since the Taylor deformation has already been dealt with in the literature for surfactants' concentration without kinetic effects or Boussinesq numbers, this section only develops theory including the former. According to the expression of $h^{(1)}$, equation (8) leads to

$$\left(-6\frac{D}{\bar{D}}\alpha H_{li}^{(1)}x_l + \zeta\alpha v_i^{*,(1)} \right) x_i = -3k_1^*\alpha H_{lm}^{(1)}x_l x_m + 3k_2^*G_{lm}^{(1)}x_l x_m \quad (38)$$

Thus

$$H_{li}^{(1)}x_l x_i = \frac{3k_2^*G_{lm}^{(1)}x_l x_m - \zeta\alpha v_i^{*,(1)}x_i}{\alpha \left(-6\frac{D}{\bar{D}} + 3k_1^* \right)} \quad (39)$$

Injecting this result in equation (10) one finally has

$$\begin{aligned} & P_{ij}\partial_j \left[\zeta P_{ik}v_k^{*,(1)} - 3P_{kl}\partial_l \left(G_{pq}^{(1)}x_p x_q \right) \right] + 2 \left(v_k^{*,(1)}n_k^{(0)} \right) \\ & = k_1^* \frac{3k_2^*G_{lm}^{(1)}x_l x_m - \zeta\alpha v_i^{*,(1)}x_i}{-6\frac{D}{\bar{D}} + 3k_1^*} - 3k_2^*G_{pq}^{(1)}x_p x_q, \quad r = R = 1 \end{aligned} \quad (40)$$

After using evolution equations,

$$-9S_{ij}^{(1)} + \frac{3}{2}T_{ij}^{(1)} + E_{ij} = 0 \quad (41)$$

$$\zeta \left(-\frac{3}{7}T_{ij}^{*,(1)} - 2S_{ij}^{*,(1)} \right) + 6G_{ij}^{(1)} = k_1^* \frac{3k_2^*G_{ij}^{(1)} - \alpha\zeta \left(6S_{ij}^{*,(1)} + \frac{3}{7}T_{ij}^{*,(1)} \right)}{-6\frac{D}{\bar{D}} + 3k_1^*} - k_2^*G_{ij}^{(1)} \quad (42)$$

we have

$$F_{ij}^{(1)} = \frac{5}{24} \frac{(19\lambda + 16 + 8Bq_\mu + 24Bq_\kappa) + 4\zeta\frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda)}{(5\lambda + 5 + 4Bq_\mu + 6Bq_\kappa) + \zeta\frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda)} E_{ij} \quad (43)$$

$$G_{ij}^{(1)} = \frac{1}{3} \frac{5(1 + \Lambda)}{(5\lambda + 5 + 4Bq_\mu + 6Bq_\kappa) + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} (1 + \Lambda)} E_{ij} \quad (44)$$

where Λ is the kinetic part and is written

$$\Lambda = \frac{1 + \frac{k_1^*}{k_2^*} \bar{\psi} \alpha}{-\frac{6}{k_2^*} + 3 \frac{k_1^*}{k_2^*} \frac{\hat{D}}{D} (1 - \bar{\psi}) - \left(1 + \alpha \frac{k_1^*}{k_2^*} \bar{\psi}\right)} \quad (45)$$

These results can be adapted to the flow used accordingly with the rate-of-strain and vorticity tensor. In simple shear flow one has

$$E_{ij} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \Omega_{ij} = \frac{1}{2} \begin{pmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \quad (46)$$

Thus, $f^{(1)}$ becomes

$$f^{(1)} = \frac{5}{8} \frac{(19\lambda + 16 + 8Bq_\mu + 24Bq_\kappa) + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} (1 + \Lambda)}{(5\lambda + 5 + 4Bq_\mu + 6Bq_\kappa) + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} (1 + \Lambda)} xy \quad (47)$$

In spherical coordinates, the Taylor deformation is then

$$D_T = \frac{Ca}{2} \left(f^{(1)}\left(\phi = \frac{\pi}{4}\right) - f^{(1)}\left(\phi = \frac{3\pi}{4}\right) \right) \quad (48)$$

$$\frac{D_T}{Ca} = \frac{5}{16} \frac{(19\lambda + 16 + 8Bq_\mu + 24Bq_\kappa) + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} (1 + \Lambda)}{(5\lambda + 5 + 4Bq_\mu + 6Bq_\kappa) + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} (1 + \Lambda)}, \quad \phi_T = \frac{\pi}{4}, \quad \theta = \frac{\pi}{2} \quad (49)$$

In the limit $\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} = 0$, $Bq_\mu = Bq_\kappa = 0$, we recover the result in Taylor (1932). In the limit $\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} = 0$, the deformation determined by Narsimhan (2019) is recovered.

3.2 Second order

According to Cox (1969), harmonics of order 2 and 4 are involved. We then define, still using Frankel decomposition, the quantities

$$\begin{aligned} P^{(2)} &= T_{lm}^{(2)} \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}, & \phi^{(2)} &= S_{lm}^{(2)} \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m} \\ P^{(2)} &= T_{lmpq}^{(2)} \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q}, & \phi^{(2)} &= S_{lmpq}^{(2)} \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q} \\ P^{*,(2)} &= T_{lm}^{*,(2)} r^5 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m}, & \phi^{*,(2)} &= S_{lm}^{*,(2)} r^5 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m} \\ P^{*,(2)} &= T_{lmpq}^{*,(2)} r^9 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q}, & \phi^{*,(2)} &= S_{lmpq}^{*,(2)} r^9 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q} \\ f^{(2)} &= F_{lmpq}^{(2)} r^5 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q}, & g^{(2)} &= G_{lmpq}^{(2)} r^5 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q} \end{aligned} \quad (50)$$

$$h^{(2)} = H_{lmpq}^{(2)} r^5 \frac{\partial^2 r^{-1}}{\partial x_l \partial x_m \partial x_p \partial x_q}$$

Since we consider a small perturbation of the drop shape, the quantities are Taylor expanded around $r = 1 + Ca f^{(1)}$. For instance the external velocity becomes

$$v_i|_{r=1+Ca f^{(1)}} = \left[Ca v_i^{(1)} + Ca^2 \left(v_i^{(2)} + f^{(1)} x_k \partial_k v_i^{(1)} \right) + o(Ca^3) \right]_{r=1} \quad (51)$$

The usual continuity equations and evolution equations are then

$$v_i^{(2)} - v_i^{*,(2)} + f^{(1)} x_k \partial_k \left(v_i^{(1)} - v_i^{*,(1)} \right) = 0 \quad (52)$$

$$\begin{aligned} & \left(\Pi_{ij}^{(2)} - \lambda \Pi_{ij}^{*,(2)} \right) n_j^{(0)} + f^{(1)} x_k \partial_k \left(\Pi_{ij}^{(1)} - \lambda \Pi_{ij}^{*,(1)} \right) n_j^{(0)} + \left(\Pi_{ij}^{(1)} - \lambda \Pi_{ij}^{*,(1)} \right) n_j^{(1)} \\ &= -\frac{1}{Ca} \left(P_{jk}^{(1)} \partial_k P_{ij}^{(1)} \right) - \frac{\hat{E} \bar{\psi}}{Ca \bar{\gamma}} \left(P_{ij}^{(0)} \partial_j \Gamma'^{(2)} + P_{ij}^{(1)} \partial_j \Gamma'^{(1)} \right) \\ &+ P_{jk}^{(0)} \partial_k \Sigma_{ij}^{*,(2)} + P_{jk}^{(0)} \partial_k \left(f^{(1)} x_m \partial_m \Sigma_{ij}^{*,(1)} \right) + P_{jk}^{(1)} \partial_k \Sigma_{ij}^{*,(1)} \end{aligned} \quad (53)$$

$$v_i^{(2)} n_i^{(0)} + f^{(1)} x_k \partial_k v_i^{(1)} n_i^{(0)} + v_i^{(1)} n_i^{(1)} = 0 \quad (54)$$

$$\begin{aligned} & \zeta P_{ij}^{(0)} \partial_j \left(P_{ik}^{(0)} v_k^{*,(2)} + P_{ik}^{(0)} f^{(1)} x_m \partial_m v_k^{*,(1)} + P_{ik}^{(0)} \Gamma'^{(1)} v_k^{*,(1)} + P_{ik}^{(1)} v_k^{*,(1)} \right) \\ &+ \zeta P_{ij}^{(1)} \partial_j \left(P_{ik}^{(0)} v_k^{*,(1)} \right) - P_{ij}^{(0)} \partial_j \left(P_{il}^{(0)} \partial_l \Gamma'^{(2)} + P_{il}^{(1)} \partial_l \Gamma'^{(1)} \right) - P_{ij}^{(1)} \partial_j \left(P_{il}^{(0)} \Gamma'^{(1)} \right) \\ &+ \zeta \left(P_{ij}^{(0)} \partial_j n_i^{(0)} \right) \left(v_k^{*,(2)} n_k^{(0)} + f^{(1)} x_m \partial_m v_k^{*,(1)} n_k^{(0)} + v_k^{*,(1)} n_k^{(1)} \right) \\ &+ \zeta \left(P_{ij}^{(0)} \partial_j n_i^{(1)} + P_{ij}^{(1)} \partial_j n_i^{(0)} \right) \left(v_k^{*,(1)} n_k^{(0)} \right) + \zeta \Gamma'^{(1)} \left(P_{ij}^{(0)} \partial_j n_i^{(0)} \right) \left(v_k^{*,(1)} n_k^{(0)} \right) \\ &= k_1^* \left(\frac{C^{(2)}}{\bar{C}} - \frac{C^{(1)} \bar{C}}{\psi} \right) - k_2^* \Gamma'^{(2)} \end{aligned} \quad (55)$$

The more detailed expressions for velocities and stress tensors are given in appendix A. The angle becomes

$$\begin{aligned}
\phi = \frac{\pi}{4} - Ca & \frac{(19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu)(2\lambda + 3)(19\lambda + 16)}{16 \left[19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right] \left[5\lambda + 5 + 6Bq_\kappa + 4Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right]} \\
& - Ca \frac{4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \left[2(2\lambda + 3)(19\lambda + 16) + \frac{\zeta}{3}(\lambda + 4)(1 + \Lambda) \right]}{16 \left[19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right] \left[5\lambda + 5 + 6Bq_\kappa + 4Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right]} \\
& - Ca \frac{4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \left(16Bq_\mu^2 + \frac{(240Bq_\kappa + 8(1 + \Lambda)\zeta + 318\lambda + 312)Bq_\mu}{3} + \frac{(282\lambda + 408)Bq_\kappa}{3} \right)}{16 \left[19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right] \left[5\lambda + 5 + 6Bq_\kappa + 4Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right]} \\
& - Ca \frac{16\zeta^2 \frac{\hat{E}^2\bar{\psi}^2}{\bar{\gamma}^2}(1 + \Lambda)^2(2\lambda + 3)}{16 \left[19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right] \left[5\lambda + 5 + 6Bq_\kappa + 4Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right]} \\
& - Ca \frac{(19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu)(46\lambda Bq_\kappa + 52\lambda Bq_\mu + 32Bq_\kappa Bq_\mu + 64Bq_\kappa + 48Bq_\mu)}{16 \left[19\lambda + 16 + 24Bq_\kappa + 8Bq_\mu + 4\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right] \left[5\lambda + 5 + 6Bq_\kappa + 4Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}}(1 + \Lambda) \right]}
\end{aligned} \tag{56}$$

By considering $\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} = 0 = Bq_\mu = Bq_\kappa = 0$ one finds the usual result for angle deviation seen in the work from Chaffey and Brenner (1967). For $\zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} = 0$ the result from Narsimhan (2019) is recovered.

4 Discussion

In this section we discuss drop deformation and deviation up to second order while considering kinetic effects.

4.1 Drop deformation

In shear flow, it is difficult to achieve a deformation slope D_T/Ca lower than 1 as stated by Taylor. However, the kinetic term involving Λ has enough freedom to obtain a smaller value. Such a condition is obtained with

$$-\frac{\bar{\gamma}}{\zeta \hat{E}\bar{\psi}} \left(\frac{19\lambda}{4} + 4 + 6Bq_\kappa + 2Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} \right) \leq \Lambda < -\frac{\bar{\gamma}}{\zeta \hat{E}\bar{\psi}} \left(\frac{15\lambda}{4} + 6Bq_\kappa - 6Bq_\mu + \zeta \frac{\hat{E}\bar{\psi}}{\bar{\gamma}} \right) \tag{57}$$

Characteristic values are plotted in figure 1 where a slope lower than 1 is indeed allowed for a given negative Λ depending on parameter's values.

By looking at the expression of Λ one finds that it may be negative if

$$\frac{2}{k_2^*} < \frac{D}{\hat{D}} \frac{k_1^*}{\alpha_2} \tag{58}$$

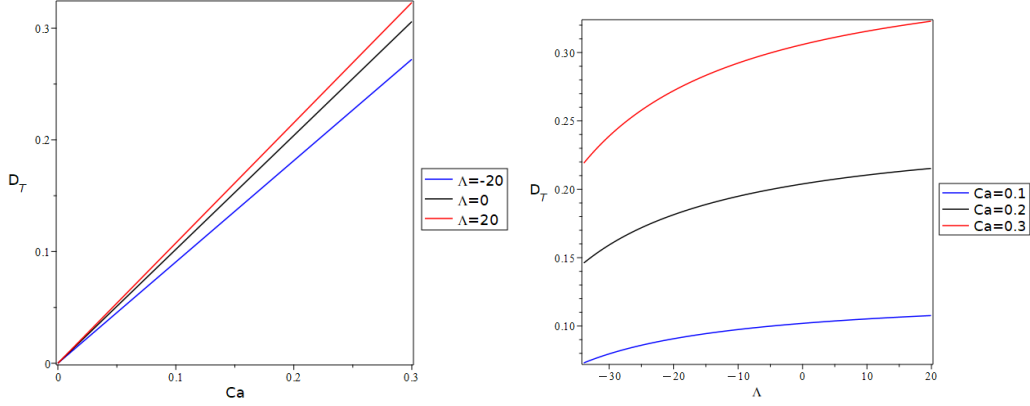


Figure 1: Drop deformation in simple shear flow at first order theory with parameters values $\lambda = 1$, $Bq_\mu = Bq_\kappa = 5$, $\zeta \hat{E} \bar{\psi} / \bar{\gamma} = 1$.

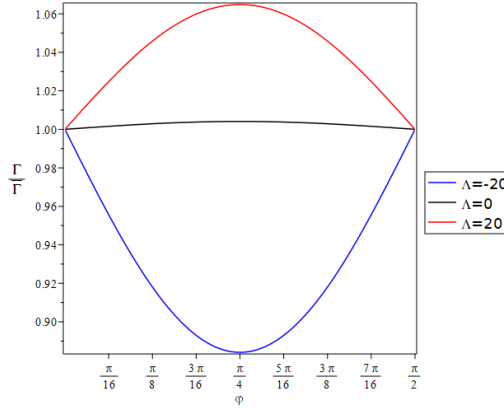


Figure 2: Dimensionless interfacial concentration of surfactants against the angle of the drop φ with $Ca = 0.1$, $\lambda = 1$, $Bq_\mu = Bq_\kappa = 5$, $\zeta \hat{E} \bar{\psi} / \bar{\gamma} = 1$.

which yields

$$2T_1 < T_D \quad (59)$$

for T_1 the characteristic adsorption time and T_D the characteristic volume diffusion time. Moreover the surface concentration is influenced by the kinetics effects leading to a decrease or increase of concentration at the extremities of the drop depending on Λ as illustrated in figure 2. It implies that the surfactants move against the imposed external flow. This counter intuitive results leads to a new perspective about surfactants' distribution and should be further investigated in experiments.

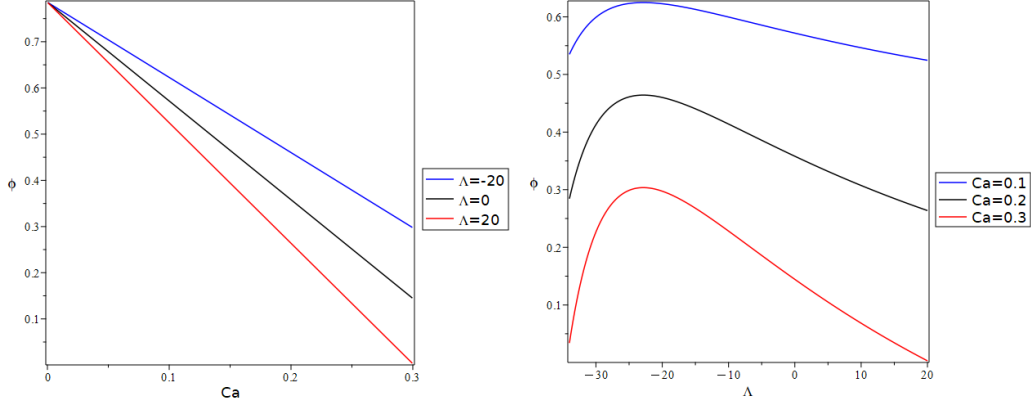


Figure 3: Angle deviation at second order theory with $\lambda = 1$, $Bq_\mu = Bq_\kappa = 5$, $\zeta \hat{E} \bar{\psi} / \bar{\gamma} = 1$.

4.2 Angle deviation

At second order, the negative values of Λ will not play a major role in the angle deviation and will only slightly counterbalance the deviation correction. As such in figure 3 the angle would be closer to $\phi = \pi/4$. The redistribution of surfactants discussed in the previous subsection will not noticeably influence the angle.

5 Conclusion

A theory for surfactants' kinetic effects was developed up to second order theory using a tensorial approach based on works from Frankel and Acrivos (1970). The consideration of adsorption of internal surfactants and desorption of interfacial surfactants' behavior led to the definition of a quantity Λ bringing a correction to the drop deformation and angle deviation in shear flow.

A small range of values is allowed for Λ to bring such corrections and change the physics of surfactants' distribution depending on the viscosity ratio, Boussinesq numbers and Stone and Leal (1990) quantity. It is possible only for an adsorption characteristic time lower than the characteristic inner diffusion time.

Hence the drop's deformation allows to be smaller than the usual Taylor deformation limit condition; kinetic effects could explain some observations made in experiments where it appears to be smaller than the common theory's prediction.

The interfacial surfactants' concentration will be higher at the semi-minor

axis' location in this situation thus moving against the induced flow. An experiment checking the behavior of interfacial surfactants' concentration should be performed to further investigate this theoretical result.

P. Regazzi would like to thank Y. Lebouazda (CPT, Marseille) for all his helpful discussions on the problem.

A Velocities and stress tensors at second order

The velocities at second order are

$$\begin{aligned} v_i^{(2)} = & 420S_{lmpi}^{(2)}x_lx_mx_p - 945S_{lmpq}^{(2)}x_lx_mx_px_qx_i - 15T_{lmpi}^{(2)}x_lx_mx_p + \frac{105}{2}T_{lmpq}^{(2)}x_lx_mx_px_qx_i \\ & + 6S_{ji}^{(2)}x_j - 15S_{lm}^{(2)}x_mx_lx_i + \frac{3}{2}T_{lm}^{(2)}x_lx_mx_i \end{aligned} \quad (60)$$

$$\begin{aligned} v_i^{*,(2)} = & 420S_{lmpi}^{*,(2)}x_lx_mx_p + \frac{294}{11}T_{lmpi}^{*,(2)}x_lx_mx_p - \frac{84}{11}T_{lmpq}^{*,(2)}x_lx_mx_px_qx_i \\ & + 6S_{ji}^{*,(1)}x_j + \frac{5}{7}T_{ji}^{*,(2)}x_j - \frac{2}{7}T_{lm}^{*,(2)}x_lx_mx_i \end{aligned} \quad (61)$$

The stress tensors are

$$\begin{aligned} \Pi_{ij}^{(2)} = & \left(2520S_{ijlm}^{(2)} - 90T_{ijlm}^{(2)}\right)x_lx_m + \left(-7560S_{jlm p}^{(2)} + 315T_{jlm p}^{(2)}\right)x_lx_mx_px_i \\ & + \left(-7560S_{ilm p}^{(2)} + 315T_{ilm p}^{(2)}\right)x_lx_mx_px_j - 1890S_{lmpq}^{(2)}x_lx_mx_px_q\delta_{ij} \\ & + \left(20790S_{lmpq}^{*,(2)} - 945T_{lmpq}^{*,(2)}\right)x_lx_mx_px_qx_ix_j + 3T_{lj}^{(2)}x_lx_i + 3T_{li}^{(2)}x_lx_j \\ & + 12S_{ij}^{(2)} - 60S_{li}^{(2)}x_lx_j - 60S_{lj}^{(2)}x_lx_i - 30S_{lm}^{(2)}x_lx_m\delta_{ij} + 210S_{lm}^{(2)}x_lx_mx_ix_j \\ & - 15T_{lm}^{(2)}x_lx_mx_ix_j \end{aligned} \quad (62)$$

$$\begin{aligned} \Pi_{ij}^* = & \left(2520S_{lmi j}^{*,(2)} + \frac{1764}{11}T_{lmi j}^{*,(2)}\right)x_lx_m - \frac{1323}{11} + T_{lmpq}^{*,(2)}x_lx_mx_px_q\delta_{ij} + \frac{252}{11}T_{jlm p}^{*,(2)}x_lx_mx_px_i \\ & + \frac{252}{11}T_{ilm p}^{*,(2)}x_lx_mx_px_j - \frac{25}{7}T_{lm}^{*,(2)}x_lx_m\delta_{ij} + 12S_{ij}^{*,(2)} + \frac{10}{7}T_{ij}^{*,(2)} + \frac{6}{7}T_{li}^{*,(2)}x_lx_j \\ & + \frac{6}{7}T_{lj}^{*,(2)}x_lx_i \end{aligned} \quad (63)$$

For the Narsimhan (2019) tensor we have

$$\begin{aligned}
\Sigma_{ij} = & Bq_\kappa \left[\left(1260S_{lmpq}^{*,(2)} + \frac{1050}{11}T_{lmpq}^{*,(2)} \right) x_l x_m x_p x_q \delta_{ij} - \left(1260S_{lmpq}^{*,(2)} + \frac{1050}{11}T_{lmpq}^{*,(2)} \right) x_l x_m x_p x_q x_i x_j \right. \\
& + \left(6S_{lm}^{*,(2)} + \frac{9}{7}T_{lm}^{*,(1)} \right) \delta_{ij} x_l x_m + \left(-6S_{lm}^{*,(2)} - \frac{9}{7}T_{lm}^{*,(2)} \right) x_l x_m x_i x_j \left. \right] \\
& + Bq_\mu \left[- \left(2520S_{lmij}^{*,(2)} + \frac{1764}{11}T_{lmij}^{*,(2)} \right) x_l x_m + \left(2520S_{lmpi}^{*,(2)} + \frac{1764}{11}T_{lmpi}^{*,(2)} \right) x_l x_m x_p x_j \right. \\
& + \left(2520S_{lmpj}^{*,(2)} + \frac{1764}{11}T_{lmpj}^{*,(2)} \right) x_l x_m x_p x_i - \left(1260S_{lmpq}^{*,(2)} + \frac{882}{11}T_{lmpq}^{*,(2)} \right) x_l x_m x_p x_q \delta_{ij} \\
& - \left(1260S_{lmpq}^{*,(2)} + \frac{882}{11}T_{lmpq}^{*,(2)} \right) x_l x_m x_p x_q x_i x_j + -12S_{ij}^{*,(2)} - \frac{10}{7}T_{ij}^{*,(2)} + \left(12S_{lj}^{*,(2)} + \frac{10}{7}T_{lj}^{*,(2)} \right) x_l x_i \\
& \left. + \left(12S_{li}^{*,(2)} + \frac{10}{7}T_{li}^{*,(2)} \right) x_l x_j + \left(-6S_{lm}^{*,(2)} - \frac{5}{7}T_{lm}^{*,(2)} \right) x_l x_m \delta_{ij} + \left(-6S_{lm}^{*,(2)} - \frac{5}{7}T_{lm}^{*,(2)} \right) x_l x_m x_i x_j \right]
\end{aligned} \tag{64}$$

References

- Barthes-Biesel, D. and Acrivos, A. (1973). Deformation and burst of a liquid droplet freely suspended in a linear shear field. *Journal of Fluid Mechanics*, 61(1):1–22.
- Chaffey, C. E. and Brenner, H. (1967). A second-order theory for shear deformation of drops. *Journal of Colloid and Interface Science*, 24(2):258–269.
- Cox, R. (1969). The deformation of a drop in a general time-dependent fluid flow. *Journal of fluid mechanics*, 37(3):601–623.
- Dupire, J., Socol, M., and Viallat, A. (2012). Full dynamics of a red blood cell in shear flow. *Proceedings of the National Academy of Sciences*, 109(51):20808–20813.
- Flumerfelt, R. W. (1980). Effects of dynamic interfacial properties on drop deformation and orientation in shear and extensional flow fields. *Journal of colloid and interface science*, 76(2):330–349.
- Frankel, N. and Acrivos, A. (1970). The constitutive equation for a dilute emulsion. *Journal of Fluid Mechanics*, 44(1):65–78.
- Frankel, N. A. (1968). *On the motion of small particles freely-suspended in laminar shearing flows*. Stanford University.

- Gounley, J., Boedec, G., Jaeger, M., and Leonetti, M. (2016). Influence of surface viscosity on droplets in shear flow. *Journal of Fluid Mechanics*, 791:464–494.
- Kaoui, B., Biros, G., and Misbah, C. (2009). Why do red blood cells have asymmetric shapes even in a symmetric flow? *Physical review letters*, 103(18):188101.
- Keller, S. R. and Skalak, R. (1982). Motion of a tank-treading ellipsoidal particle in a shear flow. *Journal of Fluid Mechanics*, 120:27–47.
- Lamb, H. (1924). *Hydrodynamics*. University Press.
- Narsimhan, V. (2019). Shape and rheology of droplets with viscous surface moduli. *Journal of Fluid Mechanics*, 862:385–420.
- Stone, H. A. (1994). Dynamics of drop deformation and breakup in viscous fluids. *Annual Review of Fluid Mechanics*, 26(1):65–102.
- Stone, H. A. and Leal, L. G. (1990). The effects of surfactants on drop deformation and breakup. *Journal of Fluid Mechanics*, 220:161–186.
- Taylor, G. I. (1932). The viscosity of a fluid containing small drops of another fluid. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character*, 138(834):41–48.
- Vlahovska, P. M., Bławdziewicz, J., and Loewenberg, M. (2009). Small-deformation theory for a surfactant-covered drop in linear flows. *Journal of fluid mechanics*, 624:293–337.
- Wailliez, J., Regazzi, P., Salonen, A., Chen, P. G., Jaeger, M., Leonetti, M., and Rio, E. (2024). Drop deformation in a planar elongational flow: impact of surfactant dynamics. *Soft Matter*.