The unsteady drag of a translating spherical drop with a viscoelastic membrane at small Reynolds number

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ABSTRACT

This manuscript quantifies the hydrodynamic drag of a spherical droplet translating in unsteady Stokes flow when the droplet has a thin, complex membrane. All forces (e.g., Stokes drag, Basset forces, unsteady memory forces, etc.) have the same functional form as the drag of a clean spherical droplet, as long as one replaces the interior viscosity with an effective (frequency-dependent) one that depends on the viscoelastic moduli of the membrane. The shear elastic moduli of the membrane do not modify the unsteady drag of the droplet – only the dilational modes matter. We demonstrate how this result can be obtained using simple symmetry/scaling arguments. The results are written for any linearly viscoelastic membrane, but we in particular examine the cases of a purely viscous membrane, purely elastic membrane, one-mode Maxwell membrane, and one-mode Kelvin–Voigt membrane. For the latter two models, we quantify how the membrane relaxation time alters the time-dependent motion of the droplet.

1. Introduction

The slow motion of a droplet in a viscous fluid is strongly affected by the absorbed molecules at its surface, which in many situations gives rise to interfacial mechanics that cannot be further described by surface tension [1,2]. There are many examples where one finds droplets with complex architectures such as solid-laden interfaces [3], vesicles [4,5], capsules [6], and lipid bilayers [7]. These systems are abundantly found in industrial and biological applications and therefore, there has been immense interest in studying these more complicated forms of soft matter over the years. Depending on the structure of these complex interfaces, additional in-plane and out-of-plane interfacial stresses can be generated, which affect the stability and motion of the droplet [8]. Here, our focus is on the in-plane friction arises from molecular components at the interface sliding over each other [9], which is known as dynamic interfacial viscosity and described by Boussinesq–Scriven constitutive model [10,11]. This phenomenon is found in concentrated layers of surfactants and lipid films and the goal of this paper is to investigate how such a membrane alters the time-dependent drag of a spherical droplet translating at low-Reynolds numbers.

The unsteady drag force on a spherical Newtonian drop is a classical problem in fluid mechanics that has been discussed in a variety of publications [12,13]. In the limit of vanishingly small Reynolds numbers (i.e., \( Re = \frac{U(t)}{v_0} \ll 1 \), where \( U(t) \) is a time-dependent translation speed, \( R \) is the droplet radius, and \( v_0 \) is the kinematic viscosity of the outer fluid), one obtains the unsteady drag force on the droplet by solving the unsteady Stokes equations for the velocity and pressure fields:

\[
\rho_0 \frac{\partial u_0}{\partial t} = \eta_0 \nabla^2 u_0 - \nabla p_0, \quad \nabla \cdot u_0 = 0
\]

\[
\rho_1 \frac{\partial u_1}{\partial t} = \eta_1 \nabla^2 u_1 - \nabla p_1, \quad \nabla \cdot u_1 = 0
\]

In the above equations, subscripts “0” and “1” represent the fluid inside and outside the droplet, while densities and viscosities are denoted by symbols \( \rho \) and \( \eta \), respectively. Following Kim and Karilla [12], this problem was solved and the drag force on a spherical droplet in the Fourier-transform domain was determined. [13] However, due to use of incorrect length scaling in the analysis, the obtained force expression was only valid for equal kinematic viscosities (\( \nu = \frac{\eta_1}{\eta_0} \) of the droplet and external fluid. Galindo et al. [14] and Lovalenti et al. [15] corrected this derivation, and the result for the drag force on a drop with radius \( R \) expressed in the Fourier-transform domain is [14]:

\[
F_D(\omega) = 6\pi\eta_0 \omega_0 R_0(\omega) \frac{1}{3 + \frac{a_1}{a_2} \frac{\eta_0}{\eta_1}} \left( 1 + \lambda_s + \frac{\lambda_s^2}{3} - \frac{(1 + \lambda_s)^2}{3 + \lambda_s + a_1 \cdot g(\lambda_s)} \right)
\]

where \( \omega \) is the frequency of oscillation and \( \lambda = \frac{\omega R^2}{\nu} \) is a non-dimensional frequency normalized by the time-scale of vorticity diffusion \( (\tau_0 = R^2/\nu) \). We note that \( \lambda \) takes different values in the interior and exterior fluid – these are denoted by \( \lambda_s \) and \( \lambda_o \), respectively. The quantity \( a_1 = \frac{a_2}{a_3} \) is the viscosity ratio between the fluids interior and

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exterior to the droplet, and the function $g(\lambda)$ is:

$$g(\lambda) = \frac{\lambda(\lambda^2 + 2)}{\lambda^2 + 2} \tan \lambda \tag{3}$$

Following Lawrence and Weinbaum [16], Eq. (2) can be re-written as the summation of the Stokes drag, Basset forces, added mass, and extra history forces. The Stokes drag is the leading term of (2) at small frequencies. At high frequencies ($|\lambda| > 1$), the force is dominated by the $O(\lambda^2)$ term, which represents the added mass. The second dominant term at large frequencies is a history term of $O(\lambda)$, which is the Basset term. [17] Thus, we have:

$$F_{\rho}(\omega) = 6\pi \eta_l R_a(\omega) \left( \frac{2 + 3q_l}{3 + 5q_l} + \frac{\eta_l}{5q_l} \lambda, \frac{\lambda^2}{9} + L(q_l, \eta_l, \lambda) \right) \tag{4}$$

where $q_l = \frac{n_c}{\sqrt{\nu_l}}$ is the ratio of kinematic viscosities and the term $L(q_l, \eta_l, \lambda)$ can be identified by comparing (2) and (4). Here, the terms are, respectively, the Stokes drag in steady uniform flow, the Basset force, the added mass force, and an additional memory term that vanishes for a solid sphere ($q_l \to \infty$). The origin of the Basset and additional memory forces is both from the growth of an unsteady boundary layer at the surface of the droplet, which arises from vorticity diffusion [16]. From the context of a spherical droplet, the additional memory contribution arises because vorticity is allowed to diffuse into the droplet’s interior fluid. In general, this force cannot be neglected when the droplet’s interface is mobile (i.e., does not obey no-slip), or if its shape is non-spherical. In the limit of a spherical rigid particle, the additional memory term vanishes and only the Basset force exists. On the other hand, for an air bubble with a clean surface, the Basset term becomes zero and the additional memory term remains.

The above analysis is for a clean droplet that lacks an interfacial layer conferring mechanical resistance to its surface (e.g., insoluble surfactants, polymer films, etc.). With this in mind, we would like to understand how a viscoelastic film on a droplet alters the time-dependent drag mentioned above. At the moment, multiple studies have investigated the steady drag of a drop with dynamic interfacial viscosities, and it turns out that the drop motion is solely impacted by dilatational surface viscosity of the interface [9,18,19]. In the steady-state limit, the translational speed is equal to that of a clean drop with a modified interior viscosity $\eta^*_l = \eta_l + \frac{n_c}{\sqrt{\nu_l}}$, which $\eta_l$ is the dilatational interfacial viscosity [9,18]. Utilizing simple scaling analysis, Narasimhan [9] demonstrated why interfacial shear viscosity is unimportant and commented on how surface concentration inhomogeneities and hydrodynamic interactions between droplets alter the main results.

The effect of surface elasticity on the unsteady motion of a spherical drop has also been of interest in the literature. In a separate study, Felderhof investigated the motion of an oscillating drop with a purely elastic membrane. [2] Utilizing a dilatational surface modulus, the author obtained a detailed expression of the frequency-dependent friction tensor for calculation of force on the drop. These obtained results agree well with expressions in the limit of a clean drop and a rigid sphere.

Here, our goal is to determine the time-dependent hydrodynamic force on a drop with a thin viscoelastic membrane in the limit of low-Reynolds numbers. Although this analysis bears some similarity to Felderhof [2], a simpler and more concise expression is derived using scaling/symmetry arguments, which reveals a compelling likeness to the solution for a clean drop, as well as important physical insights. Secondly, the force expression is extended to investigate the effect of surface viscoelasticity on the motion of a droplet, which until this point has yet to be studied. We will examine two simple viscoelastic models of the droplet membrane (single-mode Maxwell and Kelvin–Voight), although in principle any linearly viscoelastic model can be used for this analysis. Results are presented in Section 3 for the droplet’s steady drag, added mass force, Basset forces, and additional memory terms.

2. Methodology

To determine the velocity fields around a droplet with a complex membrane, we define the velocity and pressure fields as $u = \tilde{u} \exp(\text{-}i\omega t)$ and $p = \tilde{p} \exp(\text{-}i\omega t)$ and substitute the expressions into the unsteady Stokes equations (1). Furthermore, we non-dimensionalize all velocities by the translational speed $|\tilde{U}|$, lengths by the diffusion length $L_D = (\frac{\nu_l}{\partial\eta_l/\partial q_l}/2)^{1/2}$, times by $L_D/|\tilde{U}|$, and stresses by $\eta_l |\tilde{U}|/L_D$. These operations give $u = \tilde{u} |\tilde{U}|$, $\tilde{r} = \frac{r}{L_D}$, and $\tilde{p} = \frac{p}{\eta_l L_D^2 |\tilde{U}|^2}$. Here, we objects with a tilde represent non-dimensional parameters. The unsteady Stokes equations are solved subject to the following boundary conditions at the interface and far away from the drop:

$$\tilde{u}, \tilde{p} \to 0 \text{ as } \tilde{r} \to \infty$$

$$\tilde{n} \cdot \tilde{u} = \tilde{n} \cdot \tilde{U} \text{ at } \tilde{r} = \lambda_0$$

$$\tilde{u} = \tilde{u}_0 \text{ at } \tilde{r} = \lambda_0$$

$$\tilde{n} \cdot (\tilde{\sigma}_l - \tilde{\sigma}_l) \cdot \tilde{P} = [\tilde{J}_m + \tilde{J}_b] \cdot \tilde{P} \text{ at } \tilde{r} = \lambda_0$$

$$\tilde{J}_m = \lambda_0 \tilde{B}_{q_l} \tilde{V}_l \cdot [\tilde{P} \cdot (\tilde{n} \cdot \tilde{u}) - \tilde{P} \cdot (\tilde{V}_l \cdot \tilde{n}) + (\tilde{V}_l \cdot \tilde{n}) \cdot \tilde{P}^T] \cdot \tilde{P}$$

$$\tilde{J}_b = -\lambda_0 \tilde{B}_{q_l} \tilde{V}_l \cdot [\tilde{P} \cdot (\tilde{n} \cdot \tilde{u})] \tag{5}$$

In the above expressions, $\tilde{J}_m$ and $\tilde{J}_b$ are contributions from interfacial shear and dilatational viscosities given by the Boussinesq–Scriven constitutive relationship [11,20]. The quantities $\tilde{B}_{q_l} = \frac{n_c}{\nu_l}$ and $\tilde{B}_{q_l} = \frac{n_c}{\nu_l}$ are the interfacial shear and dilatational Boussinesq numbers, $\tilde{P} = \tilde{I} - \tilde{n} \cdot \tilde{n}$ is the surface projection operator, and $\tilde{V}_l = \tilde{P} \cdot \tilde{V}$ is the surface gradient.

Here, we investigate the effect of surface viscosities on the time dependent motion of a droplet using symmetry arguments that have been employed to study their steady motion [9]. If a spherical drop is subject to an external vector field $\tilde{U}$, it can be shown that the tractions from interfacial shear and dilatational viscosities scale as $\tilde{J} \sim \tilde{U} \cdot (\tilde{I} - 3\tilde{n} \tilde{n})$ since these tractions have no net force over the droplet, and the tensor $(\tilde{I} - 3\tilde{n} \tilde{n})$ is the only tensor depending on the normal vector that integrates to zero on the unit sphere. Physically, this statement arises because interfacial viscosity originates from the friction of surfactants sliding past each other, which produces equal and opposite forces that sum to zero over the droplet surface. We also note that the interfacial shear contribution scales as $\tilde{J}_m \sim \tilde{U} \cdot (\tilde{I} - \tilde{n} \tilde{n})$ since the membrane shear resistance is entirely in-plane [9]. If both of these statements are true, the interfacial shear traction must be $\tilde{J}_m = 0$ and thus the membrane’s shear moduli play no role in the dynamics (at least for a linearly viscoelastic membrane).

In contrast to the above, we find that the dilatational resistance of the membrane significantly alters the droplet’s drag. It turns out the final result can be expressed in an elegant functional form using minimal algebraic manipulations. Let the velocity field on the surface of the droplet take the following generic form, where $C_{\tilde{I}}$ and $C_{\tilde{j}}$ are constants:

$$\tilde{u} = C_{\tilde{I}} \tilde{U} + C_{\tilde{j}} \tilde{U} \cdot (\tilde{I} - \tilde{n} \tilde{n}).$$

If we evaluate the dilatational traction $\tilde{J}_b$ in Eq. (5) using this velocity field, we obtain:

$$\tilde{J}_b = \frac{2C_{\tilde{j}}}{\lambda_0} \tilde{B}_{q_l} \tilde{U} \cdot (\tilde{I} - 3\tilde{n} \tilde{n})$$

Following Kim and Karilla’s formulation[12], one can show that the tangential viscous traction on the inner surface of the drop takes the following form:

$$n \cdot \tilde{r} \cdot \tilde{J}_m = C_{\tilde{j}} \eta_l \frac{\tilde{g}(\lambda_0)}{\lambda_0} \tilde{U} \cdot (\tilde{I} - \tilde{n} \tilde{n}) \tag{7}$$

Thus, Eqs. (6) and (7) can be lumped together:

$$[n \cdot \tilde{r} + \tilde{J}_m] \cdot \tilde{P} = C_{\tilde{j}} \eta_l \frac{2 \tilde{B}_{q_l}}{\lambda_0} \frac{\tilde{g}(\lambda_0)}{\lambda_0} \tilde{U} \cdot (\tilde{I} - \tilde{n} \tilde{n}) \tag{8}$$

Comparing Eqs. (7) and (8) shows the tangential viscous traction of a droplet with a membrane (i.e., Eq. (8)) has the same functional
form as that of a clean droplet (i.e., Eq. (7)), except that one has to replace the viscosity contrast ($q_e$) with a modified one ($q_e' = \bar{q}_e + \frac{2B_{q_k}}{\bar{q}_e}$).

We note because the droplet remains spherical, the normal stress balance does not influence the derivation of the force exerted by the fluid on the droplet[15]. Thus, if one wants to determine the unsteady drag of a droplet with a thin membrane, one can use the same results as the clean droplet (i.e., Eq. (2)), but replace the viscosity ratio $q_e$ with $q_e'$. We obtain:

$$F_0(\omega) = 6\pi \eta R u(\omega) \left(1 + \lambda_0 + \frac{\lambda_0^2}{9} - \frac{(1 + \lambda_0)}{3 + \lambda_0 + q_e' \cdot g(\lambda_0)}\right)$$

(9)

This is the main result of the manuscript. We note that this analysis holds whenever the spherical droplet is under the influence of an external field described by a vector. Thus, we can use the same result (i.e., substituting $\lambda$) to quantify how a droplet’s membrane alters its motion under (a) therophoresis, (b) pressure gradient, or (c) sedimentation, and (d) electrophoresis. It should be noted that this analysis holds if the droplet remains spherical (i.e., the capillary number $Ca < 1$), and if the concentration inhomogeneities on the droplet membrane remain small. The latter holds if the surface convection of the inhomogeneities is smaller than surface diffusion, or if surface convection is weaker than adsorption/mass transfer from the bulk (i.e., weak surfactant solubility). These situations are characterized by a single dimensionless parameter called a modified surface Peclet number $Pe_{s} = \frac{\Gamma k_{s} D_{s}}{k_{b}+2D_{s}} \ll 1$, where $D_{s}$ is the surface diffusion coefficient and $k_{b}$ is the adsorption/mass transfer coefficient [21]. In the regime $Pe_{s} \ll 1$, one can show that the $O(Pe_{s})$ correction to the droplet drag follows the same formula in Eq. (9), except that one replaces the Boussinesq number by an effective one $B_{q_k}^{\text{eff}} = B_{q_k} + Pe_{s} Ma$, where $Ma$ is the Marangoni number that takes surface tension gradients into account: $Ma = \frac{-\partial \sigma}{\partial (\ln \Gamma)}$ where $\Gamma$ is the surface concentration of species [9,21]. This result is a generalization of the famous observation by Levich and others that in limited circumstances, surface tension gradients $-\partial \sigma / \partial (\ln \Gamma)$ play the same role as an effective dilatational surface viscosity [19,22].

It should also be mentioned that Eq. (9) can be extended to linearly viscoelastic membranes by replacing the Boussinesq number with a frequency dependent value (i.e., $B_{q_k} \rightarrow B_{q_k}(\omega)$), which allows one to examine how the interplay of membrane viscosity and elasticity alters the droplet drag. For the specific case when the surface dilatational viscosity is $\eta_{s} = \frac{\dot{E}_{s}}{\dot{v}_{s}}$, the drag is equivalent to the one written by Felderhof[2] for a droplet with a purely elastic membrane and elastic dilatational modulus $E$, albeit written in a much simpler manner that is extendable to the situations mentioned above. In the next section, we will examine several different linear, viscoelastic models for membrane mechanics and see how they alter droplet drag.

One last point we would like to make is that the above result reproduces the steady drag of the droplet when the dimensionless frequency $\lambda_0 \rightarrow 0$. In this case, the modified viscosity ratio becomes $q_e' = \bar{q}_e + \frac{2B_{q_k}}{\bar{q}_e}$ which agrees with earlier works by Levan [18] and Narasimhan [9]. So, in many ways, the analysis presented in this manuscript is a more general description of the problem. Lastly, if a droplet has multiple thin layers deposited on its surface, one can use the formulas above with an effective Boussinesq number that is the sum of the Boussinesq numbers of the individual phases: $B_{q_k}^{\text{eff}} = \sum_{\text{phase}} B_{q_k}^{(\text{phase})}$. One can easily derive this result through a force balance over all layers.

3. Results and discussions

In this section, we expand upon the results described previously for the droplet drag when a thin membrane is present. For now, we consider a purely viscous membrane ($B_{q_k} = \text{const}$). Here, many are interested in decomposing the forces to Stokes drag, Basset force, added mass, and additional memory terms. We re-write Eq. (9) using the definitions of these forces as described earlier in Section 1. This decomposition closely follows the suggestions by Lawrence and Weinbaum [16].

$$F_0(\omega) = 6\pi \eta R u(\omega) \left(2 + \lambda_0 + \frac{2B_{q_k}}{\bar{q}_e} + \frac{\lambda_0^2}{9} - \frac{(1 + \lambda_0)}{3 + \lambda_0 + q_e' \cdot g(\lambda_0)}\right)$$

$$+ \frac{\lambda_0^2}{9} + L'(q_e, q_{e'} \cdot B_{q_k}, \lambda_0)$$

(10)

Here, the first term is the quasi-steady Stokes drag agrees well with literature for a steady translating drop with an insoluble layer at its surface. [9,18] The second term, which is the Basset memory term, should be treated with caution. Depending on $B_{q_k}/\lambda_0$, this memory term behaves differently:

For $B_{q_k} \ll \lambda_0$, it behaves as of a clean drop ($\frac{q_{e'}}{1 + \frac{q_{e'}}{\sqrt{\lambda_0}}}$).

As $B_{q_k} \gg \lambda_0$, it takes the form of a solid sphere ($\lambda_0$).

The third term, which is the added mass, is independent of the interfacial viscosity since it is non-dissipative. Finally, the fourth term ($L'$) is the additional memory term, which is a function of the interfacial Boussinesq number and disappears in case of a rigid sphere. One can obtain $L'(q_e, q_{e'} \cdot B_{q_k}, \lambda_0)$ by comparing Eqs. (9) and (10).

To investigate these results in a time domain, notation of Yang and Leal [13] is followed and the initial value problem considered

$$U(t) = \begin{cases} 0 & ; t < 0, \\ U(0) & ; t \geq 0. \end{cases}$$

The Fourier transform can be converted to a Laplace transform $(-i\omega \rightarrow \sigma)$ and inverted. [13] The result can be represented as

$$\mathbf{G_1(\sigma)} = \frac{2 + 3q_e + 2B_{q_k}}{3 + 3q_e + 2B_{q_k}} U \quad \text{(quasi - steady drag)}$$

$$+ \int_{0}^{\sigma} G_1(\tau - \sigma) \frac{dU}{d\tau} d\tau \quad \text{(Basset memory term)}$$

$$+ \frac{1}{\nu_e} \frac{dU}{d\tau} \quad \text{(added mass term)}$$

$$+ \int_{0}^{\sigma} G_2(\tau - \sigma) \frac{dU}{d\tau} d\tau \quad \text{(additional memory term)},$$

(11)

where $i$ is the dimensionless time defined as $i = t(\lambda_0^{-1})$ and integral kernels $G$ can be determined by taking the inverse transform on associated terms in (10).

The Basset memory kernel is:

$$G_1(\sigma) = \frac{A}{\sqrt{i}}$$

(12)

which $A = \frac{q_e}{\lambda_0^{1/2} \sqrt{\nu_e}}$ for $B_{q_k} \ll 1$ and $A = 1$ as $B_{q_k} \gg 1$.

For a rigid sphere (i.e. $B_{q_k} \rightarrow \infty$ or $q_e \rightarrow \infty$), the additional memory term $G_2$ vanishes. In case of a drop, the asymptotic analysis of $G_2(i)$ gives:

$$G_2(i) = \frac{Q^2 + 2B_{q_k} + 2}{(1 + Q)^2} - \frac{P - 1}{P}$$

$$+ \frac{2q_e(1 + Q) - (Q - 2 - 2B_{q_k})^2}{(1 + Q)^2} \sqrt{\frac{i}{\lambda_0}} + O(i^{-3/2}) \text{ as } i \rightarrow 0$$

(13)

and

$$G_2(i) = \left(\frac{P - 1}{P}\right)^2 \frac{1}{\sqrt{i}} + O(i^{-3/2}) \text{ as } i \rightarrow \infty,$$

(14)

where $P = 3 + 3q_e + 2B_{q_k}$ and $Q = q_e/\sqrt{\lambda_0}$. 

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frequency dilatational viscosities, and \( \tau \) is the viscoelastic relaxation time of the membrane. Substituting \( \eta_l(\omega) \) in (9), the force expression on a drop with a simple linear viscoelastic membrane can be determined. For the drop with a simple Maxwell fluid membrane, it is seen that the force is similar to a drop with a viscous membrane with the exception of the history terms:

\[
F_D(\omega) = \frac{O(\Delta \eta_l)}{R_u(\omega)} \left( \frac{2 + 3 \eta_l + 2 B_q \eta_{1,0} + \frac{2}{9} \frac{\lambda^2}{G} + L_H(\omega)}{3 + 3 \eta_l + 2 B_q (\eta_{1,0} + \frac{1}{9} \frac{\lambda^2}{G})} \right)
\]  

(15)

where \( B_q(\omega) \) is the zero-frequency Boussinesq number of the drop surface, and \( L_H(\omega) \) is the memory contribution (Basset plus additional memory). To further investigate the history terms, it is inverted into the time domain and the memory kernel \( L_H(\omega) = G_R(\omega) + G_H(\omega) \) is derived. Fig. 2 shows the memory kernel of an air bubble and a drop with a Maxwell fluid membrane. Here, the zero-frequency Boussinesq number is \( B_q(\omega) = 5 \) and kinematic viscosity ratio of inner and outer fluids is \( \eta_{1,0} = 1 \). For the air bubble, the additional memory term only contributes to the kernel (i.e., \( L_H(\omega) = G_R(\omega) \)), which leads to a finite kernel value at \( \tau = 0 \) and a decay to zero as \( \tau \to \infty \). For zero membrane relaxation time, the membrane acts as a viscous fluid and a monotonic decrease of memory kernel \( L_H(\omega) \) over dimensionless time is observed as expected. On the other hand, a non-zero membrane relaxation time results in non-monotonic behavior (Fig. 2a).

The non-monotonic behavior is due to the competition between the following timescales: vorticity diffusion in the inner and outer fluid \( t_d = \frac{\eta_{1,0}^2}{\nu_1} \) and \( t_i = \frac{\eta_1^2}{\nu_1} + \frac{1}{\nu_1} \), the membrane’s viscoelastic relaxation time \( t_{\text{visco}} = t_\nu \), and the surface viscous time scale \( t_{\text{surf}} = \frac{\eta_{1,0}^2}{\nu_1} \). For the parameters studied here, it appears that the controlling parameter for peaks in memory spectrum is a lumped timescale \( t_{\text{lumped}} = \frac{t_{\text{surf}}}{t_{\text{visco}}} \) that depends intimately on the elasticity of the membrane and is independent of the viscosities of the bulk fluids. We typically see peaks in the spectrum at times \( t \sim t_{\text{lumped}}/t_\nu \). We suspect this situation arises because before \( t \sim O(\frac{t_{\text{lumped}}}{t_\nu}) \), there has been insufficient time for vorticity to diffuse into the bulk fluid, and energy is instead being stored in the membrane. In dimensionless terms, these conditions correspond to peaks forming at times \( t \sim \frac{1}{B_q(\omega)} \). Thus, increasing the membrane relaxation time \( \tau \) or the zero-frequency Boussinesq number \( B_q(\omega) \) shifts the peak to larger times (Fig. 2a). A shift of a peak to larger times is generally accompanied by a shorter and wider peak.

We note that the viscosity of the droplet’s interior plays a significant role in the diffusion of vorticity into the bulk fluid, and hence will alter the non-monotonic behavior of the memory kernel. In Fig. 2b, we plot the memory kernel of an equi-viscous droplet with a Maxwell membrane. In this case, the kernel contains both Basset and the additional memory contributions (i.e., \( L_H(\omega) = G_R(\omega) + G_H(\omega) \)). Non-monotonic behaviors appear less apparent when the Basset memory term does not vanish. The kernel is singular at \( \tau = 0 \), and decreases to zero as \( \tau \to \infty \).

Similar to the Maxwell model, we determine the drag force expression on a drop with a Kelvin–Voigt viscoelastic solid membrane. The drag is

\[
F_D(\omega) = \frac{O(\Delta \eta_l)}{R_u(\omega)} \left( 1 + \frac{\lambda^2}{G} + L'(\omega) \right)
\]

(16)

where \( L'(\omega) \) is the history contribution (Basset plus additional memory). The force expression is the same as a solid sphere with the exception of the history term, which is plotted in the time domain in Fig. 3. Here, the infinite-frequency Boussinesq number is \( B_q(\infty) = 0.1 \) and kinematic viscosity ratio of inner and outer fluids is \( \eta_{1,0} = 1 \). For the case of an air bubble (Fig. 3a), the memory kernel is equal to the additional memory term since the Basset term is zero (i.e., \( L_H(\omega) = G_H(\omega) \)). Depending on the value of the membrane relaxation time, the curve can form one or more local extrema before going to zero as \( \tau \to \infty \). As before, we find that the location of the extrema occur at times \( t \sim \frac{1}{B_q(\omega)} \). In this situation, there has been insufficient time for the diffusion of vorticity to
dominate the memory spectrum, which allows the membrane viscoelasticity to give rise to peaks and troughs. The location of the local minima and maxima shifts to longer times as the relaxation time increases and the infinite-frequency Boussinesq number decreases. Fig. 3b shows the memory kernel for an equi-viscous drop, which is singular at $t = 0$ since both the Basset history and additional memory terms contribute (i.e., $L_{q_0}(t) = G_B(t) + G_d(t)$). In this case, the memory kernel appears to monotonically decrease towards zero as $t \to \infty$.

In principle, the analysis provided in this study can be utilized to identify some of the rheological characteristics of a single droplet translating in a bulk fluid. For example, the dilatational Boussinesq number of a droplet can be determined from a steady Stokes drag measurement, and the membrane relaxation time can be identified from the time-dependent drag, in particular the memory kernel (i.e., the drag minus the Stokes and added mass contributions). For the specific case of an air bubble, additional peaks in the memory kernel occur at cross-over times that can be fitted numerically using the formulas in Eq. (9). When small surface concentration inhomogeneities are present, one can use an effective Boussinesq number in this fitting. Although it is yet to be seen whether this approach is practical, it is interesting to note that one can only measure dilatational moduli using this technique, since shear moduli does not alter droplet drag.

4. Conclusions

We have quantified the time-dependent drag force on a spherical droplet with a thin membrane at low Reynolds numbers. Using symmetry arguments, we discussed why the membrane’s shear elastic modulus is unimportant in the calculation of the unsteady drag, and how the membrane’s dilatational modulus alters the unsteady drag force on a translating spherical droplet.

The main result of this manuscript is an expression for the unsteady drag force on a drop with a viscous membrane (Eq. (0)), which has the same functional form as an accelerating clean droplet but with a modified viscosity ratio. In other words, if one wants to obtain the hydrodynamic force on a droplet with a complex membrane, one can examine the force expression of a clean droplet and simply replace the interior viscosity contrast ($q_0$) with a modified one ($q_0^* = q_0 + \frac{2}{\gamma} B_{q_{eq}}$, where $B_{q_{eq}}$ is the membrane’s dilatational Boussinesq number. It should be noted that this result is valid if (a) the droplet Reynolds number remains small ($Re < < 1$), (b) the droplet remains nearly spherical (i.e., $Ca < < 1$), and (c) concentration inhomogeneities on the droplet membrane remain small. For a surfactant-covered interface, the latter condition holds if the modified surface Peclet number is small ($Pe_s = \frac{2 \gamma}{Re^2 + D_K/R} \ll 1$, where $D_K$ is the surface diffusion coefficient and $K$ is the adsorption constant). We note that one can use this analysis when the droplet is under the action of any field described by a single vector, which is common during startup flows involving pressure gradients, sedimentation, and/or thermophoresis.

The transient force expressions developed in this paper are decomposed into the familiar Stokes drag, Basset forces, added-mass forces, and additional memory terms following the methods in Lawrence and Weinbaum [16]. In the time-domain for a purely viscous membrane, it is noticed that the memory kernel (i.e., the sum of Basset forces plus
additional memory contributions) is always positive and decreases monotonically over time. In case of an air bubble at finite interfacial Bousinesq numbers, the history term is finite as \( t \to 0 \). As the inner viscosity ratio \( (\eta_i) \) increases or \( BQ_k \to \infty \), the memory kernel becomes singular at \( t = 0 \).

Additionally, we extend the results to capture the effect of membrane viscoelasticity on the transient motion of the droplet. The results are valid for any linearly viscoelastic membrane, but here we examined three specific cases: (a) purely elastic membrane, (b) a one-mode Maxwell membrane, and (c) a one-mode Kelvin–Voigt membrane. For a purely elastic membrane, the force expression is equivalent to the one derived by Felderhoff, [2] albeit written in a more concise manner. For a viscoelastic membrane, we quantified how the droplet’s membrane relaxation time alters the time-dependent drag, in particular, the transient viscous terms (i.e., sum of Basset and additional memory forces). It is shown that the history term may not monotonically decrease in time depending on the membrane’s relaxation time. The competition between the membrane’s relaxation time and the diffusion timescale of vorticity plays a role in this behavior.

There are many avenues that have yet to be explored regarding this study. Two future lines that can be addressed are the effect of non-uniform interfacial viscosity that often arises due to concentration inhomogeneities from flow [26,27], as well as the effect of surface rheology on the droplet motion outside the small deformation regime. Lastly, the stability and breakup of a droplet with a complex membrane is an area that is only recently being addressed [1]. Such topics will be pursued in future publications.

Conflict of Interest

The authors do not have a conflict of interest to report.

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Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jnmfm.2019.06.008.

References