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C. Sorgentone* **- A.-K. Tornberg***

NUMERICAL SIMULATION OF 3D SURFACTANT-COVERED DROPS IN A STRONG ELECTRIC FIELD

Abstract. The numerical literature for 3D surfactant-laden drops placed in electric fields is extremely limited due to the difficulties associated with the deforming drop surfaces, interface conditions and the multi-physics nature of the problem. Our numerical method is based on a boundary integral formulation of the Stokes equations and the leaky-dieletric model; it is able to simulate multiple drops with different viscosities covered by an insoluble surfactant; it is adaptive in time and uses special quadrature methods to deal with the singular and nearly-singular integrals that appear in the formulation. In this proceeding we will show how the method is able to maintain a high quality representation of the drops even under substantial deformations due to strong electric fields.

1. Introduction

There is currently a growing interest in the applications of electric-field induced dynamics on deformable particulate suspensions. Biomedical applications span from separation and detection, to selective manipulation, drug delivery and so on [1]. Other engineering applications are represented by mixed emulsions where a specific material needs to be isolated as a water-in-oil emulsion where high-viscosity oils combined with asphaltenes or resins (or in general substances that behave like surfactants) make it hard to extract the water and an electric field can be applied to accelerate the sedimentation process. The study and understanding of the physics of these systems is then necessary to design apposite biotechnological devices for the above mentioned purposes.
The influence of either surfactants or electric fields on drops have been largely studied in 2D, whilst in 3D the literature is not so wide. The combined effect of surfactants together with electric fields is however a new and almost unexplored area of research [5]. A detailed summary of the available literature can be found in [8], where we developed a highly accurate method for the numerical simulation of these systems. It is a challenging problem due to the multi-physics involved and the complex moving geometries, especially for objects such as drops or bubbles that present a deformable interface (and then respond differently in electric field as compared with solid particles).
In this proceeding we will show the robustness of the method presenting simulations of surfactant-covered drops placed in strong electric fields, both uniform and linear.

*KTH Royal Institute of Technology, Department of Mathematics, 10044 Stockholm, Sweden

2. Mathematical formulation

Below we use some standard notation in electrohydrodynamics, whose definitions can be found, for example, in [10].
We consider N drops suspended in an ambient fluid. The Stokes equations read

$$\begin{cases} -\mu_i \Delta \mathbf{u}(\mathbf{x}) + \nabla P(\mathbf{x}) = 0 \\ \nabla \cdot \mathbf{u}(\mathbf{x}) = 0 \end{cases} \tag{2.1}$$

for every $\mathbf{x}$ inside the i-th drop ($i = 1, \ldots, N$) or in the exterior region ($i = 0$), where $\mathbf{u}$ is the fluid velocity, P is the pressure and μ_i is the viscosity. The fluid motion is coupled to the interface motion via the kinematic boundary condition

$$\dot{\mathbf{x}} = \mathbf{u}(\mathbf{x}), \quad \text{for all } \mathbf{x} \in S^*, \tag{2.2}$$

where $\mathbf{x}$ is the position vector and $S^* = \bigcup_i S_i$ denotes the union of all drop surfaces. The permittivity ε and the conductivity σ are discontinuous across the interface. A stress balance at the interface establishes the flow and electric field interaction:

$$\left[\left[\mathbf{n} \cdot (\Sigma^{el} + \Sigma^{hd})\right]\right]_{S^*} = \mathbf{f} \tag{2.3}$$

where $[[\cdot]]_{S^*}$ denotes the jump across the interface (e.g., $[[\sigma]]_{S_i} = \sigma_0 - \sigma_i$), $\mathbf{n}$ is the outward pointing unit normal, Σ^{el} is the electric stress, Σ^{hd} is the hydrodynamic stress. Denoting by $\gamma = \gamma(\mathbf{x})$ the interfacial tension, the interfacial force is defined by:

$$\mathbf{f} = 2\gamma(\mathbf{x}) H(\mathbf{x}) \mathbf{n}(\mathbf{x}) - \nabla_S \gamma(\mathbf{x}), \tag{2.4}$$

where $H = \frac{1}{2} \nabla_S \cdot \mathbf{n}$ denotes the mean curvature and $\nabla_S = (I - \mathbf{nn})\nabla$ is the surface gradient. For a clean drop, the surface tension coefficient $\gamma(\mathbf{x})$ will be constant, and the second term in (2.4), the so-called Marangoni force, will vanish.
The electric stress Σ^{el} is given by the Maxwell stress tensor, defined as,

$$\Sigma^{el} = \tilde{\varepsilon} \varepsilon_0 (\mathbf{E} \otimes \mathbf{E} - \frac{1}{2} \|\mathbf{E}\|^2 \mathbf{I}) \tag{2.5}$$

where $\tilde{\varepsilon}$ is the permittivity of the vacuum and $\mathbf{E}$ denotes the electric field; the hydrodynamic stress tensor is given by

$$\Sigma^{hd} = -PI + \mu(\nabla \mathbf{u} + \nabla \mathbf{u}^T). \tag{2.6}$$

To solve for the drop evolution under flow and electric fields, we use a boundary integral equation (BIE) method.
Using the non-dimensionalization described in [8], equations (2.1) and (2.3) can be reformulated as the following boundary integral equation:

$$\begin{aligned} (\lambda_i + 1)\mathbf{u}(\mathbf{x}_0) = &- \sum_{j=1}^{N} \left(\frac{1}{4\pi} \int_{S_j} \left(\frac{\mathbf{f}(\mathbf{x})}{Ca_E} - \mathbf{f}^E(\mathbf{x}) \right) \cdot G(\mathbf{x}_0, \mathbf{x}) dS(\mathbf{x}) \right) \\ &+ \sum_{j=1}^{N} \left(\frac{\lambda_i - 1}{4\pi} \int_{S_j} \mathbf{u}(\mathbf{x}) \cdot T(\mathbf{x}_0, \mathbf{x}) \cdot \mathbf{n}(\mathbf{x}) dS(\mathbf{x}) \right), \quad \text{for all } \mathbf{x} \in S^* \end{aligned} \tag{2.7}$$

where $\mathbf{f}$ was defined in (2.4), $\mathbf{f}^E$ is the electric force on the interface $\mathbf{f}^E = \left[\!\left[\mathbf{n}\cdot\Sigma^{el}\right]\!\right]_{S^*}$, Ca_E is the electric capillary number and $\lambda_i = \frac{\mu_i}{\mu_0}$ denotes the viscosity contrast of the i-th drop. The tensors G and T are the Stokeslet and the Stresslet ones,

$$G(\mathbf{x}_0,\mathbf{x}) = I/r + \hat{\mathbf{x}}\hat{\mathbf{x}}/r^3, \quad T(\mathbf{x}_0,\mathbf{x}) = -6\hat{\mathbf{x}}\hat{\mathbf{x}}\hat{\mathbf{x}}/r^5, \tag{2.8}$$

with $\hat{\mathbf{x}} = \mathbf{x}_0 - \mathbf{x}$ and $r = |\hat{\mathbf{x}}|$. It is important to remark that at $\mathbf{x} = \mathbf{x}_0$, the kernels G and T have a singularity, and the integrals are to be understood as principal value integrals. It should also be noted that when $\mathbf{x}$ is very close to one drop surface, we have a quasi-singularity; this means that the computation of the corresponding integral must be performed by using a rule that takes into account this quasi-singularity. Thus, all integrals of the above type must be computed by using proper quadrature formulas, that take the above singular and quasi-singular behaviors into account, as better explained in the next section.

In the present paper we consider that the surfactant-covered drops are subjected to the electric field $\mathbf{E}_\infty$ applied far away from the drop, where $\mathbf{E}_\infty = \mathbf{E}_\infty(\mathbf{x})$ is defined on the whole space, and in particular we will consider uniform and linear fields. The electric field is described by the *leaky–dielectric* model, in which the electric charges are assumed to be present only at the interface and not in the bulk. The boundary value problem for the electric field can be written as:

$$-\nabla\cdot\mathbf{E} = 0 \quad \text{in} \quad \mathbb{R}^2\backslash S^* \tag{2.9a}$$

$$[\![\sigma E_n]\!]_{S^*} = 0 \tag{2.9b}$$

$$\mathbf{E}(\mathbf{x}) \to \mathbf{E}_\infty(\mathbf{x}) \quad \text{as} \quad |\mathbf{x}| \to \infty \tag{2.9c}$$

where $E_n = \mathbf{E}\cdot\mathbf{n}$ is the normal component of $\mathbf{E}$. For simplicity we will assume the viscosity ratio $\lambda = \frac{\mu_i}{\mu_0}$, the conductivity ratio $R = \frac{\sigma_i}{\sigma_0}$ and the permittivity ratio $Q = \frac{\varepsilon_i}{\varepsilon_0}$ to be the same for all the drops, $i = 1,\ldots,N$. Using these definitions, eq. (2.9b) implies

$$E_n^0 = RE_n^i. \tag{2.10}$$

We will henceforth omit the superscript 0 for the normal component of the electric field.

Denoting by $\mathbf{E}_t = (I - \mathbf{nn})\cdot\mathbf{E} = \mathbf{E} - E_n\mathbf{n}$ the tangential components of $\mathbf{E}$, the electric force on each interface i can be written in terms of E_n and $\mathbf{E}_t$ [4]:

$$\mathbf{f}^E = \left[\!\left[\mathbf{n}\cdot\Sigma^{el}\right]\!\right]_{S^*} = \frac{\tilde{\varepsilon}\varepsilon_0}{2}[(1-\frac{Q}{R^2})E_n^2 - (1-Q)E_t^2]\mathbf{n} + \tilde{\varepsilon}\varepsilon_0(1-\frac{Q}{R})E_n\mathbf{E}_t. \tag{2.11}$$

The electric force on the membrane needs to be computed by solving (2.9) for a given drop shape. Since (2.9) is a linear partial differential equation, similar to the fluid problem, we can recast it using a boundary integral formulation [4]:

$$\mathbf{E}_\infty(\mathbf{x}_0) - \sum_{j=1}^{N}\int_{S_j}\frac{\hat{\mathbf{x}}}{4\pi r^3}[\![E_n(\mathbf{x})]\!]dS(\mathbf{x}) = \begin{cases}\mathbf{E}^i & \text{if } \mathbf{x}_0 \text{ inside } S^*,\\ \frac{1}{2}[\mathbf{E}^0 + \mathbf{E}^i] & \text{if } \mathbf{x}_0 \in S^*,\\ \mathbf{E}^e & \text{if } \mathbf{x}_0 \text{ outside } S^*.\end{cases} \tag{2.12}$$

Eq. (2.12) exactly satisfies the far-field condition (2.9c) and gives an integral equation for E_n by taking its inner product with the normal vector and using (2.10):

$$\frac{R}{R+1}\mathbf{E}_\infty \cdot \mathbf{n}(\mathbf{x}_0) + \frac{R-1}{R+1}\sum_{j=1}^{N}\int_{S_j}\frac{\hat{\mathbf{x}}\cdot\mathbf{n}}{4\pi r^3}E_n(\mathbf{x})dS(\mathbf{x}) = \frac{1}{2}E_n(\mathbf{x}_0). \tag{2.13}$$

The tangential component of the electric field is given by

$$\mathbf{E}_t = \frac{\mathbf{E}^0+\mathbf{E}^i}{2} - \frac{1+R}{2R}E_n\mathbf{n}. \tag{2.14}$$

The presence of an insoluble surfactant on the drop surface will affect the interfacial tension γ. It is related with the surfactant concentration by the equation of state. Different equations of state can be used, as the Szyszkowski equation (also called Langmuir equation of state) which is given, in dimensionless form, by:

$$\gamma(\Gamma) = 1 + E\ln(1 - x_s\Gamma) \tag{2.15}$$

where E is the elasticity number and x_s is the surface coverage, $0 \leqslant x_s \leqslant 1$. The equation governing the evolution of the surfactant concentration is a convective-diffusion equation given in dimensionless terms by:

$$\frac{\partial\Gamma}{\partial t} + \nabla_S\cdot(\Gamma\mathbf{u}_t) - \frac{1}{Pe}\nabla_S^2\Gamma + 2H(\mathbf{x})\Gamma(\mathbf{u}\cdot\mathbf{n}) = 0, \tag{2.16}$$

where Pe is the Péclet number.
To summarize, given the initial shape of the drop and the initial surfactant concentration, we need to solve the system composed by eqs. (2.2)-(2.9)-(2.16) with boundary condition (2.3), where the solution for the velocity $\mathbf{u}$ and the electric field $\mathbf{E}$ is obtained via the boundary integral formulations presented (respectively eq. (2.7) and (2.13)) and the interfacial tension is updated via the equation of state (2.15).

3. Numerical Method

We will use a Galerkin formulation to solve the system composed by eqs. (2.7,2.13,2.16). The numerical method is described in details in our previous papers [7, 8]. Here we will just summarize the main numerical tools we have used to apply the above formulation. These are:

- *Spherical Harmonics expansion representation:*
  All the variables (position vector, surfactant concentration, electric field) will be represented by a spherical harmonics expansion truncated at order p:

$$y_p(\theta,\phi) = \sum_{n=0}^{p}\sum_{m=-n}^{n} y_n^m Y_{nm}(\theta,\phi), \tag{3.17}$$

  where $\{(\theta,\phi) : \theta\in[0,\pi], \phi\in[0,2\pi)\}$ and Y_{nm} are the normalized scalar spherical harmonic functions of degree n and order m.

- *Regular, singular and nearly-singular integration:*
  The quadrature rule for regular integrals is defined as follows:

$$\int_S y d\gamma \approx \sum_{j=0}^{p} \sum_{k=0}^{2p+1} w_j y(\theta_j, \phi_k) W(\theta_j, \phi_k), \tag{3.18}$$

  where $w_j = \frac{\pi}{p} \frac{w_j^G}{sin(\theta_j)}$ and $W(\theta_j, \phi_k)$ is the infinitesimal area element of the surface S.
  As already mentioned in the previous section, when computing the integrals in (2.7), (2.12), and (2.13) we need a special treatment for the singular ($\mathbf{x}_0 = \mathbf{x}$) and the nearly-singular ($lim_{\mathbf{x}_0 \to \mathbf{x}}$) cases. These two situations have a very different nature: in the first case it is an analytical problem (the integrand itself is not properly defined at the singular value) while in the second case it is a purely numerical issue. In both cases the integrals must be computed using proper numerical strategies: we will treat the two situations separately, exploiting the fact that spherical harmonics are eigenfunctions of the Laplace operator on the sphere [3,9] for the singular case, and using an interpolation technique for the nearly-singular case [7].

- *Time-stepping:*
  The ODE system one obtains for the drop/surfactant, after having applied the above mentioned (discretized) Galerkin method, is evolved in time using the combination of the Midpoint Rule for the evolution of the drops with an Implicit-Explicit (IMEX) second-order Runge-Kutta scheme for the evolution of the surfactant concentration. This choice allows to treat the convective term that appears in the surfactant evolution equation (2.16) explicitly, and the diffusive term implicitly. To make the implicit part of the solver efficient also for large diffusion coefficients, a preconditioner is designed taking advantage of spherical harmonics eigenfunction properties [7]. The overall scheme is adaptive with respect to drop deformation and surfactant concentration as explained and showed in [6].

- *Reparametrization:*
  Significant distortions of the point distributions representing the drops surfaces may arise, especially when simulating 3D drops under the influence of a strong electric field. This can easily lead to aliasing errors and numerical instabilities and, for this reason, a reparametrization procedure is absolutely necessary. We developed a spectrally accurate algorithm able to ensure good quality of the surface representation also in the case of strong distortions and able to handle the surfactant concentration which lives on the surfaces of the drops. A detailed explanation of the procedure can be found in [7].

4. Results

All the following simulations are performed for an initially spherical drop of radius 1 with uniform surfactant concentration and viscosity ratio $\lambda = 1$. In Fig. 1 it is shown the

simulation run with spherical harmonic expansion order $p = 11$ for a single surfactant-covered drop placed in a uniform electric field $\mathbf{E}_\infty = Ca_E(0,0,1)$, where Ca_E is the electric capillary number. The surfactant parameters are set to: $x_s = 0.36$, $Pe = 100$ and $E = 0.2$. We can see that the drop assumes a prolate shape and at the tips of the drop the surfactant concentration is lower than on the rest of the surface; this is because the drop didn't reach a steady state.
We compared our numerical experiments finding good agreement with the simulations presented in [2], where a single clean drop is placed in a strong linear field $\mathbf{E}_\infty = Ca_E(-x,-y,2z)$. However it's worth mentioning that Deshmukh and Thaokar assume the axisymmetric simplification which is valid only for a drop placed in the origin; we don't have this restriction. In Fig. 2a we show the simulation presented in [2] Fig. 10c with the same physical parameters and $Ca_E = 0.5$. The final time is $T = 0.5$, while in Fig. 2b we changed the permittivity ratio to $Q = 0.1$ and the final time is $T = 0.1$. Note also that in Fig. 2b the particle is not centered in the origin and for this reason the resulting electric field is much stronger. For both the simulations we set $p = 15$.
Finally we also show two surfactant-laden drops interacting in a linear field with $R = 5$, $Q = 0.5$, $Ca_E = 0.6$ at the final time $T = 0.2$ run with $p = 11$. The particles are set in a symmetric setting and then also the surfactant concentration takes a symmetric configuration. The two particles interacting in the electric field generate a translation velocity that, with these physical parameters, results to be attractive.

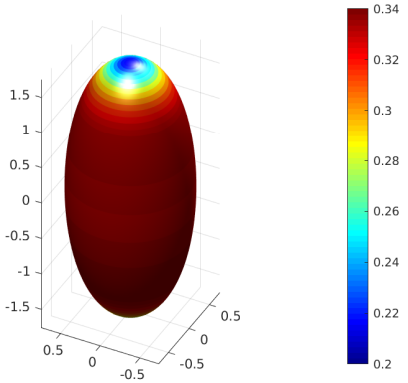
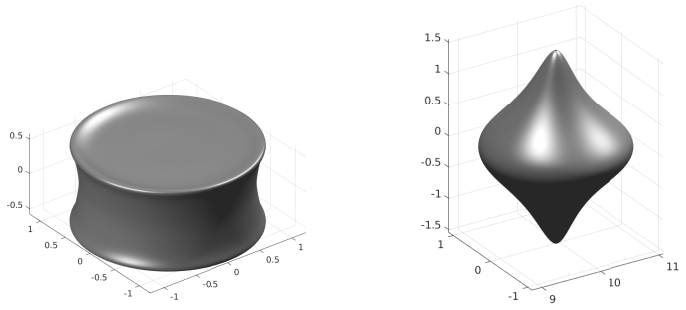


Figure 1: A single surfactant covered drop in a uniform electric field at time $T = 1$. For this simulation $Ca_E = 2$, $R = 20$, $Q = 2$ and $p = 11$. The colorbar denotes the surfactant concentration.

4.1. Conclusions

In our previous works [7, 8] we presented a highly accurate numerical method for simulating multiple surfactant-covered drops placed in electric fields, where we validated



(a) (b)

Figure 2: a) A single clean drop placed in a linear field with $R = 1$, $Q = 20$, $Ca_E = 0.5$ at the final time $T = 0.5$ run with $p = 15$.; b) Same as in a) but with $Q = 0.1$, showed at the final time $T = 0.1$.

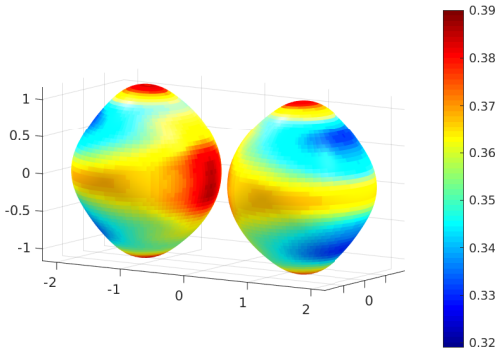


Figure 3: Numerical simulation of two surfactant-covered drop in a linear electric field with $R = 5$, $Q = 0.5$, $Ca_E = 0.6$ at the final time $T = 0.2$ run with $p = 11$. The surfactant parameters are the same of the simulation in Fig. 1 and the colorbar denotes the surfactant concentration.

our code against experimental, numerical and theoretical results for the physical situations where the capillary number is below the critical one. In this proceeding we showed three numerical simulations of clean and surfactant-covered drops to illustrate the robustness of our method even when the particles are under the influence of strong electric fields. In all the presented cases the deformation is very pronounced but still the method is able to capture the electrohydrodynamic of the drops keeping the order of the spherical harmonics expansions reasonably small (never higher then $p = 15$) and the error in the volume conservation is never above 6e-05.

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Chiara SORGENTONE, Anna-Karin TORNBERG,
Department of Mathematics, KTH Royal Institute of Technology
10044 Stockholm, SWEDEN
e-mail: sorgento@kth.se, akto@kth.se

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