

COUPLING OF POISSON-BOLTZMANN EQUATION WITH STOKES SYSTEM: THE FORMATION OF RAYLEIGH JETS

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Abstract. We develop a Boundary element method to study the formation and evolution of Rayleigh jets in electrically charged droplets. In order to develop it, we couple Stokes hydrodynamic system with the electrokinetic equations for the distribution of charges under the Poisson-Boltzmann approximation. We estimate the velocity and radius of the jet as a function of the various physical parameters in the system

1 INTRODUCTION

Rayleigh jets appear from charged droplets once the charge overcomes some critical value. In the case of a perfectly conducting liquid, the critical charge Q is such that the Rayleigh fissibility ratio X (cf. [8]), defined as

$$X = \frac{Q^2}{32\gamma\pi^2\varepsilon_0 R_0^3}, \quad (1)$$

is larger than 1. In (1), γ is the surface tension coefficient, R_0 is the radius of the drop and ε_0 is the dielectric constant outside the drop.

When the drop's charge is overcritical, the drop deforms into a prolate spheroid (cf. [3], [6], [7] for experimental results and [1], [2] for numerical simulations) and conical tips tend to develop at the regions of maximum curvature. When the fluid is a perfect conductor and is modeled under Stokes approximation, it was shown in [1], [2] that conical tips develop in finite time (see Figure 1). These conical tips, called dynamic Taylor cones, present a semiangle around $20^\circ - 25^\circ$, which coincides almost exactly with the experimental measurements. Nevertheless, in the experimental observations, very fast and thin jets are produced from the conical tips (see figures 1). This is a fact that cannot be reproduced in [2], [1] under the Stokes and perfect conductor assumptions. For perfect fluids, jets have been reported recently in [5]. Nevertheless, for very small drops (of the order of $100 \mu\text{m}$ or smaller), Reynolds number can be very small (of the order of 10^{-4} or smaller), so that it seems necessary to investigate the formation of jets under Stokes approximation. Our hypothesis is that it is the finite electric conductivity and the presence of Debye layers in electrolyte solutions what induces the production of Rayleigh jets. The first effect, finite conductivity, implies that electric charges do not move infinitely fast inside the liquid medium. The second effect, finiteness of Debye layer, implies that positive and negative charges do not balance exactly inside the drop so that the liquid is electrically neutral at the bulk of the fluid. Instead, they form a thin layer (the so-called Debye layer) where there is a nonzero net charge.

We will show in this article that the hypothesis sketched above does indeed lie at the heart of the formation of Rayleigh jets and will be used to compute the jet's main characteristics such as velocity and size. Our results will also be used to discuss Rayleigh jet's features dependence on temperature and ion concentration.

2 Modelling

In microfluidics, relevant physical dimensions are sufficiently large in comparison to atomic scales that it is permissible to treat the fluid as if it were a continuum. Thus, the fluid velocity \mathbf{v} and pressure p are regarded as continuous functions of position \mathbf{x} and time t , and they obey the incompressible Navier-Stokes equations with external body forces \mathbf{F}_e acting per unit volume (e.g., gravity, electric, electromagnetic or centrifugal force).

$$\rho_0 (\partial_t \mathbf{v} + \mathbf{v} \cdot \nabla \mathbf{v}) = -\nabla p + \mu \Delta \mathbf{v} + \mathbf{F}_e. \quad (2)$$

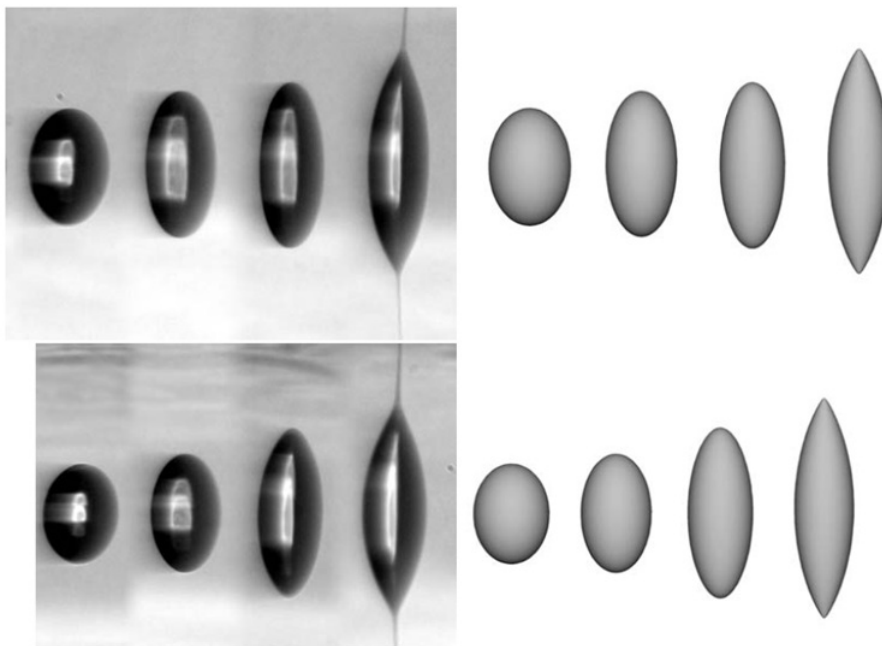


Figure 1: Deformation of a viscous drop and formation of Rayleigh jets. Taken from [2]; experiments by Grimm and Beauchamp.

This is supplemented by the continuity equation which takes into account the fact that in a liquid the density changes are slight:

$$\nabla \cdot \mathbf{v} = 0. \quad (3)$$

In the above, ρ_0 is the (constant) density of the fluid, μ the viscosity constant, p the pressure and \mathbf{v} the flow velocity. The first equation (2) is the momentum equation and is an expression of Newton's second law of motion. The second equation (3) is the continuity equation expressing conservation of mass.

The relative size of the term on the left of equation (2) (due to fluid inertia) and the second term on the right (due to viscosity) is characterized by the Reynolds number

$$Re = \frac{UL\rho_0}{\mu},$$

where U and L denote a characteristic velocity and length for the flow. In most applications of microfluidics, $Re \ll 1$, in some applications, $Re \sim 1$. By contrast, in large scale flows (aircraft engines, geophysical flows etc.) $Re \gg 1$. We will consider masses of fluid at a very small length scale so that $Re \ll 1$ and the left hand side of (2) which corresponds to fluid inertia can either be neglected, or treated as a small perturbation. In the former case, we arrive at the Stokes flow equations:

$$-\nabla p + \mu \Delta \mathbf{v} + \mathbf{F}_e = 0, \quad (4)$$

which is often referred to as slow, creeping or highly viscous flow. All of these terms mean the same thing, namely $Re \ll 1$. The unknown scalar field p in (4) is determined by the constraint provided by (3).

Electrokinetic refers to mechanical effects that arise due to the motion of ions in liquids. The working fluid in microfluidic systems is normally water which contains ions of both signs due to dissociated water molecules or other ionic components: acids, salts, and molecules with dissociable charged groups. Normally, a volume element of such a fluid considered “infinitesimal” in the continuum view point still contains a sufficiently large number of ions of either sign for statistical fluctuations to be unimportant for the fluid element to be considered charge neutral. Therefore, the net algebraic transfer of momentum due to any ambient electric field is also zero (even though a non-zero electric current may exist in the fluid due to the ordered motion of these ions). Electrokinetic effects arise when this balance of positive and negative charges is disturbed due to external factors as we studied when we considered the Poisson-Boltzmann equation. In the macroscopic description, the fluid in the so called Debye Layer, experienced an electrical force with volume density $\mathbf{F}_e = \rho \mathbf{E}$ with ρ the electric charge density, and $\mathbf{E} = -\nabla V$ the local electric field with V the electric potential.

Let us consider now a droplet $\Omega(t)$ of a viscous incompressible fluid containing ions electrically charged, the droplet is suspended in a dielectric and also incompressible viscous fluid $\Omega^*(t) \setminus \overline{\Omega(t)}$, which is in contact with electrodes to zero potential, and which we would like to take infinite. In this case, the boundary $\partial\Omega(t)$ will move with the flow, so we have to take into account also the exterior fluid dynamic.

The mathematical formulation corresponding to the model of the electric potential V in $\Omega^*(t)$ that consists of an electrolytic droplet $\Omega(t)$ surrounded by a dielectric fluid $\Omega^*(t) \setminus \overline{\Omega(t)}$, is the Poisson-Boltzmann equation

$$-\nabla \cdot (\varepsilon_0 \varepsilon_r \nabla V) = \rho \equiv \sum_{i=0}^{N-1} e z_i c_i e^{-\frac{e z_i}{k_B T} V} \text{ in } \Omega^*(t), \quad (5)$$

where ρ is the electric charge, due to N charged species (ions or free electrons), with valencies z_i . e , k_B and T are the electron charge, Boltzmann constant and absolute temperature respectively. The constants c_i can be found from the total amount of each of the species.

We had assumed that the droplet contains a net amount of electric charge Q , so if we denote σ the surface charge density in the droplet $\Omega(t)$, we know that $\sigma(\mathbf{x}, t) = -\varepsilon_0 \varepsilon_r \frac{\partial V}{\partial \mathbf{n}} \Big|_{\partial\Omega(t)}$ and satisfies

$$\int_{\partial\Omega(t)} \sigma(\mathbf{x}, t) dS(\mathbf{x}) = Q. \quad (6)$$

Q constant in time because of the charge conservation law.

Then the model governing the liquid flow in the droplet $\Omega(t)$ and in the exterior fluid is the Stokes system including the electric body force per unit volume $\rho \mathbf{E} = -\rho \nabla V$ in the

momentum equation for the droplet:

$$-\nabla p^{(1)}(\mathbf{x}, t) + \mu_1 \Delta \mathbf{v}^{(1)}(\mathbf{x}, t) + \rho(\mathbf{x}, t) \mathbf{E}(\mathbf{x}, t) = 0 \quad \mathbf{x} \in \Omega(t), \quad (7)$$

$$-\nabla p^{(2)}(\mathbf{x}, t) + \mu_2 \Delta \mathbf{v}^{(2)}(\mathbf{x}, t) = 0 \quad \mathbf{x} \in \Omega^*(t) \setminus \overline{\Omega(t)}, \quad (8)$$

$$\nabla \cdot \mathbf{v}^{(k)}(\mathbf{x}, t) = 0 \quad \mathbf{x} \notin \partial\Omega(t), \quad k = 1, 2, \quad (9)$$

where $\mathbf{v}^{(k)}$ is the velocity field, $p^{(k)}$ is the pressure, μ_k the viscosity for $k = 1, 2$, the respective inner and outer fluids.

The normal component of the velocity has to be continuous across the boundary and we need

$$\mathbf{v}^{(1)} \cdot \mathbf{n} = \mathbf{v}^{(2)} \cdot \mathbf{n} \equiv \mathbf{v} \cdot \mathbf{n} \quad \text{on } \partial\Omega(t).$$

The dependence on t comes from the motion of the boundary $\partial\Omega(t)$ given by the equation

$$\frac{d\mathbf{x}}{dt} \cdot \mathbf{n} = \mathbf{v}(\mathbf{x}, t) \cdot \mathbf{n}, \quad (10)$$

with \mathbf{n} exterior to $\Omega(t)$, expressing the fact that the surface of the drop moves in the direction of its normal, following the normal component of the velocity field.

$$\Delta \mathbf{f} = (\mathbf{T}^{(2)} - \mathbf{T}^{(1)}) \mathbf{n} = \gamma \kappa \mathbf{n}, \quad (11)$$

where γ is the surface tension coefficient, κ the mean curvature, and

$$T_{ij}^{(k)} = -\delta_{ij} p^{(k)} + \mu_k \left(\frac{\partial v_i^{(k)}}{\partial x_j} + \frac{\partial v_j^{(k)}}{\partial x_i} \right) \quad k = 1, 2.$$

It is important to notice that the force $\rho \mathbf{E}$ can be written as

$$\rho \mathbf{E} = -f(V) \nabla V \equiv -\nabla F(V),$$

where $f(V)$ is the right hand side of (5). Then, we can redefine the pressure inside the drop as

$$P^{(1)} = p^{(1)} + F \circ V, \quad (12)$$

and move the electric effect into the boundary condition, so that the new hydrodynamic system reads

$$-\nabla P^{(k)}(\mathbf{x}) + \Delta \mathbf{v}^{(k)}(\mathbf{x}) = 0 \quad \mathbf{x} \in \Omega_k, \quad (13)$$

$$\nabla \cdot \mathbf{v}^{(k)} = 0 \quad \mathbf{x} \in \Omega_k, \quad (14)$$

$$(\mathbf{T}^{(2)} - \mathbf{T}^{(1)}) \mathbf{n} = (\gamma \kappa + (F \circ V)) \mathbf{n} \quad \text{on } \partial\Omega_1, \quad (15)$$

$$\mathbf{t}^t (\mathbf{T}^{(2)} - \mathbf{T}^{(1)}) \mathbf{n} = \mathbf{0} \quad \text{on } \partial\Omega_1, \quad (16)$$

$$\mathbf{v} \longrightarrow \mathbf{0} \quad \text{as } |\mathbf{x}| \longrightarrow \infty. \quad (17)$$

In [4] it was shown that the solution to Poisson-Boltzmann equation, in the case of a binary ionic solution (such as Na^+Cl^-) is such that

$$\begin{aligned} F(V) &= -\frac{(\sigma_0(x_S) + \varepsilon\sigma_1(x_S))^2}{2} + \kappa(\mathbf{x})|\sigma_0(x_S) + \varepsilon\sigma_1(x_S)|\varepsilon + O(\varepsilon^b), \\ &\sim -\frac{\sigma_0(x_S)^2}{2} - \varepsilon\sigma_0(x_S)\sigma_1(x_S) + \kappa(\mathbf{x})|\sigma_0(x_S)|\varepsilon + O(\varepsilon^b), \end{aligned}$$

in terms of

$$\varepsilon = \frac{\varepsilon_0\varepsilon_r k_b T l}{(ez)^2}, \quad l = (Vol)^{\frac{1}{3}},$$

provided $\varepsilon \ll 1$. $\sigma_0(x_S)$ is the surface charge density for the perfect conductor (that is, when the potential at $\partial\Omega(t)$ is constant in space) and

$$\sigma_1(x_S) = -2\frac{\int_{\partial\Omega} \mathcal{N}(\ln(\sigma_0))}{Q}\sigma_0(x_S) + 2\mathcal{N}(\ln(\sigma_0)) + O(\varepsilon) \quad (18)$$

with \mathcal{N} the Dirichlet to Neumann operator restricted to $\partial\Omega(t)$. The functions $\sigma_0(x_S)$ and $\mathcal{N}(\ln(\sigma_0))$ are related to the Laplace equation in $\mathbb{R}^3 \setminus \bar{\Omega}(t)$, with $\Omega(t) \subset \mathbb{R}^3$ the region that the electrolytic droplet occupies.

3 Boundary integral formulation

The velocity field solving Stokes system is such that, at a point $\mathbf{x}_0 \in \partial\Omega(t)$,

$$v_j(\mathbf{x}_0) = \frac{-1}{4\pi(\mu_1 + \mu_2)} \int_{\partial\Omega} G_{ij}(\mathbf{x}, \mathbf{x}_0) f_i(\mathbf{x}) dS - \frac{\mu_2 - \mu_1}{4\pi(\mu_1 + \mu_2)} \int_{\partial\Omega}^{PV} v_i(\mathbf{x}) T_{ijk}(\mathbf{x}, \mathbf{x}_0) n_k(\mathbf{x}) dS(\mathbf{x}), \quad (19)$$

with

$$\begin{aligned} G_{ij}(\mathbf{x}, \mathbf{x}_0) &= \frac{\delta_{ij}}{|\mathbf{x} - \mathbf{x}_0|} + \frac{(x_i - x_{0,i})(x_j - x_{0,j})}{|\mathbf{x} - \mathbf{x}_0|^3}, \\ T_{ijk}(\mathbf{x}, \mathbf{x}_0) &= -6\frac{(x_i - x_{0,i})(x_j - x_{0,j})(x_k - x_{0,k})}{|\mathbf{x} - \mathbf{x}_0|^5}, \end{aligned}$$

for $i, j, k \in \{1, 2, 3\}$ and where

$$\begin{aligned} f_i(\mathbf{x}) &= (\gamma\kappa + F(V))n_i \\ &= \left(\gamma\kappa - \frac{(\sigma_0(x_S))^2}{2} - \varepsilon\sigma_0(x_S)\sigma_1(x_S) + \kappa(\mathbf{x})|\sigma_0(x_S)|\varepsilon \right) n_i, \end{aligned}$$

corresponding to the boundary condition (15). On the other hand the operator \mathcal{N} , providing the normal derivative of a solution to Laplace equation outside $\Omega(t)$ from the boundary data, in (18) can be obtained from the integral equation

$$u(\mathbf{x}_0) = -\int_{\partial\Omega} G(\mathbf{x}, \mathbf{x}_0) \frac{\partial u}{\partial \mathbf{n}}(\mathbf{x}) dS(\mathbf{x}) + \int_{\partial\Omega} [u(\mathbf{x}) - u(\mathbf{x}_0)] \frac{\partial G(\mathbf{x}, \mathbf{x}_0)}{\partial \mathbf{n}} dS(\mathbf{x}), \quad (20)$$

where $G(\mathbf{x}, \mathbf{x}_0)$ is the fundamental solution to Laplace's equation.

We solve (19), (20) by discretization of the integral into subintervals. Then we solve the resulting linear systems for $v_j(\mathbf{x}_0)$ and $\frac{\partial u}{\partial \mathbf{n}}(\mathbf{x})$. More details on the procedure can be found in [1].

4 Numerical results: the evolution of a droplet

Using the boundary condition we can compute the flow, and then obtain the evolved droplet $\partial\Omega(t + \Delta t)$ using

$$\frac{d\mathbf{x}}{dt} = \mathbf{v} \cdot \mathbf{n},$$

and continue recursively.

Now we will find out the stability of the electrolytic droplets in terms of ε , that corresponds to the Debye Length.

4.1 Stability analysis

Using the algorithm we found that the critical charge (relative to the critical charge for $\varepsilon = 0$) is, as a function of the ε :

Table 1: Relative critical charge

| ε | 0 | 0.02 | 0.03 | 0.04 | 0.05 | 0.06 | 0.07 |
|-------------------------------------|---|--------|--------|--------|--------|--------|--------|
| $\frac{Q_{c,\varepsilon}}{Q_{c,0}}$ | 1 | 1.0494 | 1.0750 | 1.1011 | 1.1278 | 1.1551 | 1.1829 |
| X_ε | 1 | 1.1012 | 1.1556 | 1.2124 | 1.2719 | 1.3343 | 1.3993 |

If we take a charge greater or equal than the critical charge for the respective case of ε , we have instability.

Fitting quadratically we obtain

$$\frac{Q_{c,\varepsilon}}{Q_{c,0}} = 2.8288\varepsilon^2 + 2.4147\varepsilon + 1,$$

with a residual 0.00050.

Our conclusion is the following: The critical charge increases with ε . This fact agrees with the observation in [3] that water droplets, containing always a certain amount of ions, are able to hold an amount of charge slightly larger than Rayleigh's limit (that is, $Q_{c,0}$).

4.2 The jets

We take a value of charge that exceeds the critical charge we can see a deformation in the droplet, different than those observed in the numerical experiments that considered the perfect conductor case.

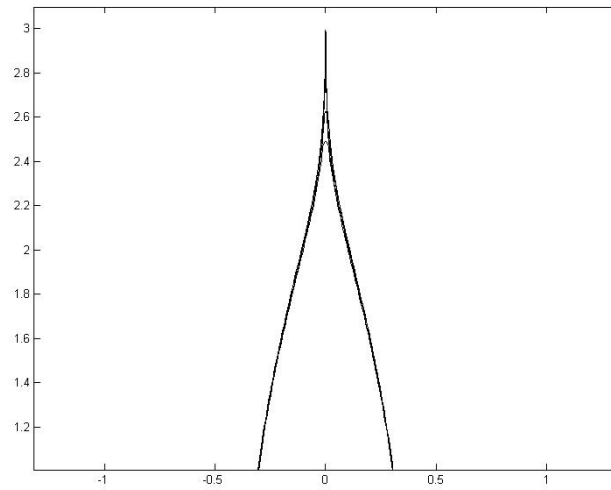


Figure 2: The formation of jet from an electrically charged viscous droplet. Top: numerical simulation from our model. Bottom: experiment from Grimm and Beauchamp.

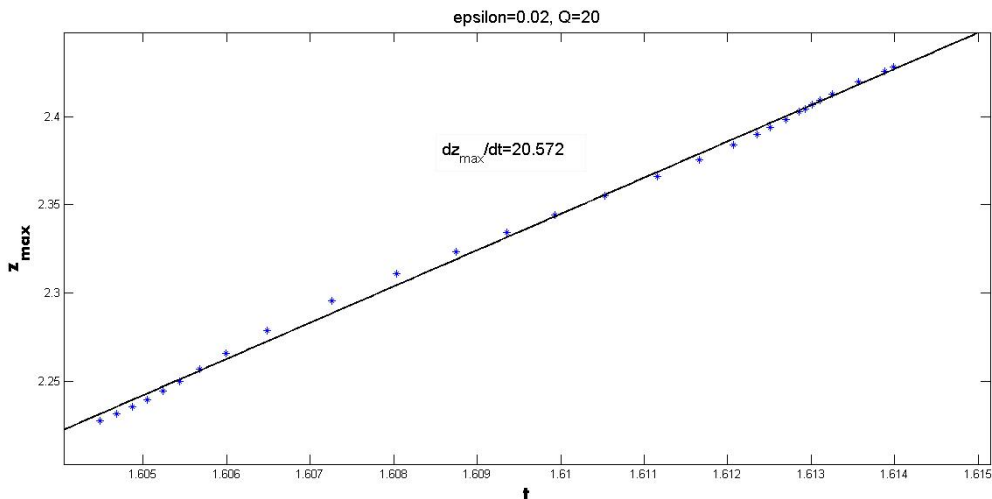


Figure 3: Position of the jet’s tip vs time and linear fit.

4.3 The velocity and radius of the jets

It is necessary to define what a “jet” is, but before of doing it, we can take some outputs and analyze the velocity. Observe in Figure 2 the presence of jets as observed in the experiments reported, for instance, in [3], [6].

Next, we will analyse, based on numerical simulations and asymptotic analysis, the main features of these jets as a function of ε (which is proportional to the absolute temperature) and ion concentration.

As we can observe, jets are emitted with a constant velocity (see Figure 3. If we plot the velocity of the jet v_j as a function of ε , we can detect a scaling law

$$v_j = \frac{1}{\varepsilon}, \tag{21}$$

so that jets are emitted faster as ε decreases. Of course, very large velocities as $\varepsilon \rightarrow 0$ are not realistic, since inertial terms that have been neglected under Stokes approximation would then become dominant. Nevertheless, (21) provides an important qualitative result: the jet’s velocity is inversely proportional to ε . Notice that in the limit $\varepsilon = 0$, which corresponds to the perfect conductor, the velocity becomes singular as shown in [1], [2] with the formation of a conical tip. It is then expected that the radius of the jet collapses to zero as $\varepsilon \rightarrow 0$. A clear cone-jet structure can be observed: a cone whose vertex connects with a thin jet. By mass conservation, the flux of mass across a cross-section of the cone (which is essentially independent of ε as the jet develops) equals the flux of mass over a cross-section of the jet. Therefore, if the radius of the jet is r_j , then

$$\rho\pi r_j^2 v_j = Const.,$$

which implies, by (21), a jet's radius

$$r_j \propto \varepsilon^{\frac{1}{2}}. \quad (22)$$

Since, for a given solution, ε is proportional to the absolute temperature, we can conclude that the jet's radius decreases when Debye layer's thickness decreases. This is a common experimental observation in the electrokinetic context.

5 CONCLUSIONS

A boundary element method has been developed for the study of the hydrodynamics and electrokinetics in charged droplets. The drop is a ionic solution with free electrons and the distributions of positive and negative charges is modelled by Poisson-Boltzmann equation. We find Rayleigh jets from our numerical method and show that their size and velocity depend on various physical parameters. More specifically, we introduce a dimensionless parameter ε , proportional to Debye's length relative to drop's size. When ε approaches zero, we recover the limit of perfect conductors.

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