Electrospray from Magneto-electrostatic Instabilities

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1 Introduction and Background

An electric field, applied to the free surface of a conducting or dielectric liquid, causes electrohydrodynamic (EHD) stresses that distort the surface. If the EHD stresses are high enough the distortion results in a "Taylor cone" that sprays droplets and/or ions via electrospray. A magnetic field applied to a magnetic fluid similarly produces ferrohydrodynamic (FHD) stresses that cause analogous distortion of the free surface. In work reported here we create superparamagnetic fluids with varying electrical conductivity and subject these fluids to combined EHD and FHD stresses. These fluids are synthesized by stabilizing magnetic nanoparticles in ionic liquids and other low-volatility fluids.

This abstract describes an integrated experimental, theoretical, and numerical investigation of electrospray from combined EHD/FHD instabilities in ionic liquid ferrofluids (ILFFs) that is designed to uncover the governing processes in this new phenomenon. The goal of this work is to quantify how the combination of electric and magnetic surface stress components affect electrospray behavior in a superparamagnetic liquid.

2 Ferro- electrohydrodynamic Surface Deformation

Prediction of the onset voltage for ILFF electrospray is complicated by two factors: (1) The electric and magnetic stresses act in concert and both depend strongly on the shape of the meniscus, and (2) the fluid free surface deforms gradually under the applied fields such that there is no relevant "tip diameter" that can be used to estimate the onset electric field. One sub-goal of our research was to numerically simulate the steady state behavior of a droplet of conductive ferrofluid in the presence of electric and magnetic fields and use the results of the simulation to understand the component contributions to the meniscus deformation. To validate the accuracy of the numerical simulation, results were compared against images of the ferrofluid meniscus under matching field conditions.

The fluid selected for this study was commercially available EFH1 manufactured by Ferrotec. This is a surfactant-stabilized light-hydrocarbon-based ferrrofluid. The equilibrium geometry of the deformed meniscus is described by the magnetic and electrically augmented Young-Laplace equation along the interfacial boundary. This relationship for a fluid interface subject to EHD and FHD stresses is:

$$\Delta p + \underbrace{\frac{1}{2}\mu_0\left(M\cdot\hat{n}\right)^2 + \mu_0\int_0^H M\,dH}_{\text{Magnetic}} + \underbrace{\frac{1}{2}\varepsilon_0\left(E\cdot\hat{n}\right)^2}_{\text{Electric}} = -\sigma\left(\nabla_t\cdot\hat{n}\right)$$

where Δp is the pressure jump across the meniscus, $\hat{n}$ is the surface unit normal, σ is the coefficient of surface tension, M is the fluid magnetization, and E, H are the electric and magnetic fields. COMSOL Multiphysics was used to perform the simulations of the ILFF in the presence of electric and magnetic fields. To construct the model, the two-phase flow – moving mesh, electrostatics, and magnetostatics – no current interfaces were utilized. The two-phase flow moving mesh interface utilizes the arbitrary Lagrangian-Eulerian (ALE) method, which allows for very precise tracking of the fluid interface., and consequently good knowledge of the fields at the interface. The electric and magnetic fluid stress tensors were added to the interface balance through the use of a weak contribution along the interfacial boundary.

To determine the accuracy of the numerical model, an imaging apparatus was designed to obtain silhouette images of a ferrofluid droplet under controllable electric and magnetic fields. A Helmholtz coil was utilized to generate a variable uniform magnetic field and electrodes were used to apply electric fields. Simulation results, together with image data, are shown in Figure 1. The agreement verifies our surface stress model and allows us to identify and study individual contributions to the surface stress. It is noteworthy that the FHD stress contains the magnetic analogue $\frac{1}{2}\mu_0(M\cdot\hat{n})^2$ to the EHD stress $\frac{1}{2}\varepsilon_0(E\cdot\hat{n})^2$, but also contains a new magnetic pressure term given by $\mu_0\int M\,dH$ that does not have an EHD analogue. The results of combined EHD/FHD stress is shown in Figure 2, where it is apparent that both the magnetic and electric fields play a strong role in the deformation of the meniscus and eventual spray onset.

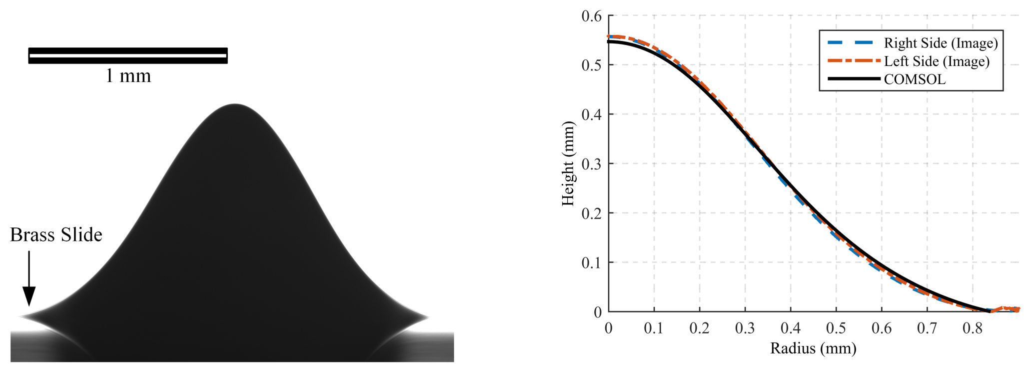

Figure 1. (Left) Silhouette image of ferrofluid droplet on a flat plate subject to FHD surface stress. A uniform vertical magnetic field has been applied via Helmholtz coil. (Right) Comparison of image profile with microfluidic numerical simulation performed using COMSOL.

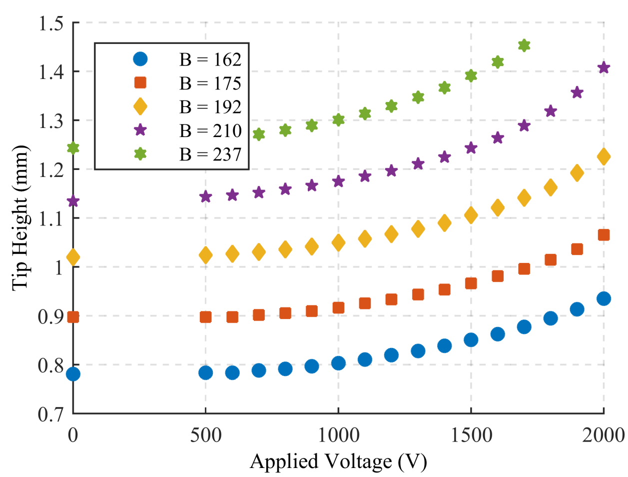

Figure 2. Meniscus deflection of a ferrofluid under combined EHD/FHD as a function of both applied magnetic and electric fields. Magnetic field, *B*, is indicated in the legend in units of Gauss. Data were obtained by analyzing silhouette images such as that shown in Figure 1 (left).

3 Magnetically-augmented Electrospray

In this work we explore the stability domain of FHD-augmented electrospray with moderate electrical conductivities in the Taylor cone electrospray mode, with a special focus on determining the smallest achievable flow rates, which in turn yield the smallest possible drops. All ferrofluids in this work were prepared by Jain and Hawkett with sterically stabilized Fe_2O_3 nanoparticles (d=25 nm) suspended in sulfolane.

Rather than inducing electrospray from a sessile drop or open pool such as presented in Figs. 1 and 2, we chose to spray the ferrofluid from the tip of a sharpened capillary in a conventional configuration. This allows us to isolate the effects due only to the magnetic field/fluid interaction and to directly compare with the large volume of capillary data. To supply a magnetic field to the spray tip two annular solenoids are aligned in series with a gap in their middle for visualization. A silica capillary (OD 360 μm ID 70 μm) is sharpened to a tip (tip OD 85 μm) and introduced along the central axis of the solenoids. Using 20% Fe_2O_3 (by mass) sulfolane ferrofluid provided by Jain and Hawkett, solutions of EAN in sulfolane were prepared to increase the conductivity of the ferrofluid but maintain magnetite concentration across samples; pure EAN, 10% EAN in sulfolane, and 1% EAN in sulfolane were used to produce ferrofluids with 10%, 1%, and 0.1% EAN respectively and each with 18% magnetite by mass. These fluids have conductivities of 0.324, 0.033, and 0.012 S/m respectively.

Figure 3 (Left) shows representative data for the 1% EAN mixture. For each of the three magnetic conditions shown the data point with the lowest flow rate indicates the minimum flow for which a stable electrospray cone could be maintained: further reduction in flow rate causes sporadic and pulsatile emission. The introduction of a magnetic field while electrospraying moderately conducting ferrofluids results in a drastic expansion of the range of conditions permitting a steady cone jet: with no magnetic field the minimum stable flow was approximately 80 nL/h, but when a 295-Gauss field was added the flow could be reduced to 35 nL/h while still exhibiting stable emission. Figure 3 (Right) demonstrates the dependence of normalized (to zero field) minimum stable flow rate on magnetic field strength. Another observation of note is the somewhat drastic shifts in the Taylor cone phase space in voltage and flow rate: for instance at 100 nL/h with a 295-Gauss magnetic field the emitted current is approximately 130 nA, while the zero-B-field case emits only 90 nA.

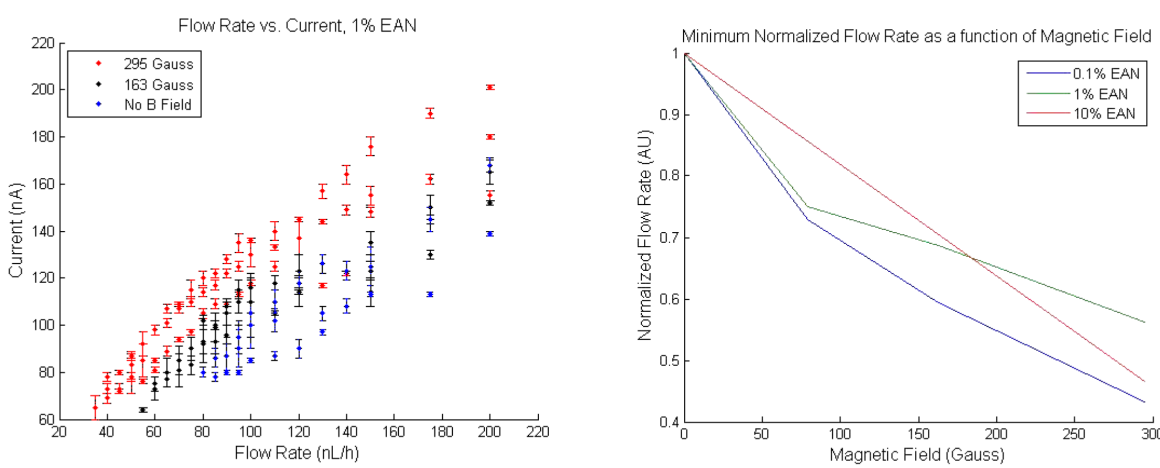

Figure 3. (Left) Current-flow-rate behavior of capillary electrospray from sulfolane ferrofluid and 1% EAN. The addition of FHD stress is seen to dramatically shift the minimum achievable flow rate. (Right) Minimum stable flow rate (normalized to the zero magnetic field minimum flow rate) for a range of ferrofluid conductivities.

Some considerations on the current-vs.-flow-rate curves obtained for the magnetized case follow. The tip curvature of the electrified cone is much sharper than for the purely magnetic situation. Therefore, one would expect that the behavior in the tip region where the electrified jet forms would be unaffected by the magnetic field, simply because electric stresses are dominant in this region. This expectation is, however, not met by our measurements, with a substantial vertical shift of the current at a given voltage resulting from application of a magnetic field. This vertical shift cannot be understood on the basis of our prior well established theoretical explanation for the mechanism driving the current in a Taylor cone.[*] A considerable effort will accordingly be required to rationalize the observed change in the I(Q) curve as well as the associated minimum flow rate.

4 Spray Modeling

Molecular Dynamics (MD) simulation is a mature computational method for simulating the equilibrium properties of a many-body system such as a spray of ILFF molecules and nano-particles. Since the EHD/FHD electrospray phenomenon is completely dominated by the chemical atomistic behavior of the ionic liquid as it is injected into strong fields, the only reliable method for capturing the highly nonequilibrium chemical, electrical, and magnetic interactions is through the use of MD.

An all-atom simulation of ionic liquid electrospray currently requires 0.3 million atoms, which makes the simulation computationally expensive. To lower the computational cost, we use the Effective Field Coarse Graining (EFCG) method by Wang and Voth.[†] The principle idea behind EFCG is to aggregate all the non-essential atoms and degrees of freedom as a single coarse-grained site or “bead”. As an example, for the EAN molecule, we postulate that the hydrogen atoms and their corresponding degrees of freedom with the carbon atom of the methyl group (CH3) do not have a significant effect on the electrospray process. Therefore it can be simplified to as a single site. Similarly, the methylene group, the ammonia group, and the nitrate group, are simplified to sites.

To perform MD simulations, the inside of a platinum capillary, 57 Å in radius and 275 Å in length, is populated with the number of molecules of the selected IL, corresponding to the selected IL’s number density. The IL molecules are then allowed to equilibrate to room temperature using a canonical ensemble or NVT for the first 0.5 million iterations followed by the next 0.5 million iterations using microcanonical ensemble or NVE (keeping the number of particles, volume, and energy of the system fixed). An electric field is then applied between the tip of the capillary and an extractor region, 1000 Å away from the tip, using the *fix efield* command in LAMMPS. The flow of IL through the capillary is generated using a repulsive wall. Using the moving wall and an electric field of 0.5 V/nm, we were able to recreate the formation of the Taylor’s cone in LAMMPS, as shown on the RHS of Fig. 4.

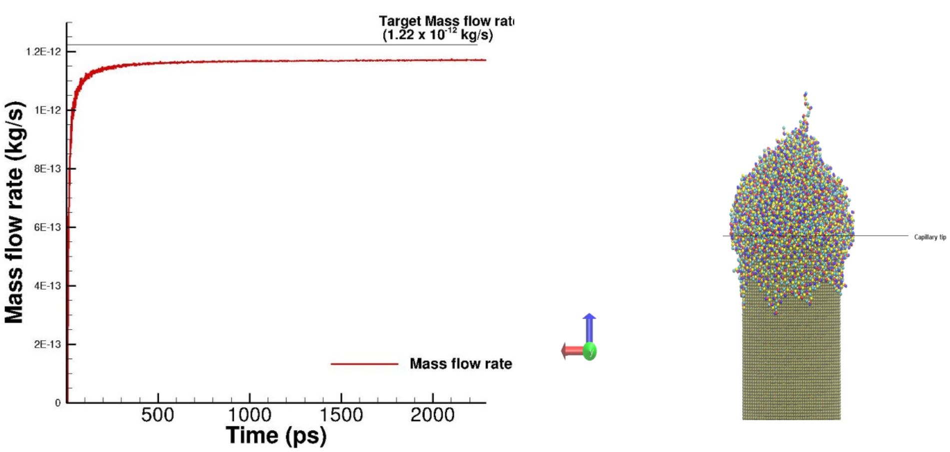

Figure 4. Generating mass flow using repulsive wall potential in LAMMPS and Taylor’s cone formation for EMIM-BF4.

[*] J. Fernández de la Mora, and I. G. Loscertales, The current emitted by highly conducting Taylor cones, J. Fluid Mechanics, **260**, 155-184, 1994.

[†] Wang, Y. and Noid, W.G. and Voth, G.A., *Effective Field Coarse Graining*, **Physical Chemistry Chemical Physics**, vol. 11**,** 2009.