Hierarchical Colloidal Vortex Rings in a Constant Electric Field

Yilong Han and David G. Grier
The James Franck Institute, Institute for Biophysical Dynamics, and Department of Physics
The University of Chicago, 5640 S. Ellis Ave., Chicago, IL 60637
(Dated: March 31, 2012)

Despite nearly two centuries of study, the response of charged particles dispersed in water to the influence of electric fields can be quite surprising, particularly when the particles also interact strongly with each other. This article describes a previously unrecognized class of hierarchically organized dynamical patterns that arise in the bulk of charge-stabilized colloidal suspensions when electrohydrodynamic forces due to constant applied fields complete with gravity.

Our system, shown schematically in Fig. 1(a), resembles that previously used [1, 2] to study interfacial colloidal electrokinetic phenomena. An aqueous suspension of monodisperse colloidal silica spheres 3.0 µm in diameter (Bangs Laboratories, Lot No. 4740) is confined to a 4×1.5 cm² horizontal layer H = 200±5 µm thick between a glass cover slip and a glass microscope slide. Both inner glass surfaces are coated with 10 nm thick gold electrodes on 10 nm thick titanium wetting layers. While still optically thin, these electrodes have a resistivity of less than 50 Ω/□ and allow us to apply uniform vertical electric fields to the confined suspension. Once equilibrated to pH 5.5 in air, the colloidal silica spheres have a surface charge density of roughly −0.4 mC/m² [3]. Given their density of 2 g/cm², they sediment rapidly onto the lower electrode.

Positively biasing the upper electrode by less than 2.4 V has little effect because ions in solution screen out the electric field. Sustained upward forces only occur at higher biases for which hydrolysis at the electrodes feeds steady-state ionic fluxes, which in turn exert electroviscous forces on the charged spheres [2, 4]. These fluxes are spatially uniform in the parallel plate geometry, so that the drag they exert on an isolated sphere is independent of height, h, in the cell. Consequently, well separated spheres (< 0.01 monolayer) rise straight to the upper electrode at biases high enough to overcome gravity.

Charged spheres not only respond to ionic fluxes, but also distort them, and the distortions mediate long-range inter-sphere interactions [2]. These interactions drive new cooperative behavior appears in denser monolayers. Increasing the bias beyond 2.6 V levitates the sedimented monolayer of spheres into hundreds of extraordinary flower-like clusters such as the example in Fig. 1(a), all floating freely at h = 40 µm above the lower electrode. Each cluster consists of a rapidly circulating toroidal vortex in which spheres travel downward along the inner surface and return upward along the outside, completing one cycle in a few seconds. Most often, the dense ring of spheres is surrounded by a diffuse circulating corona that extends outward for tens of micrometers. Although these clusters somewhat resemble conventional laminar vortex rings [5], they are driven by quite different mechanisms [4]. In particular, each cluster’s circulation is consistent with a central downward flux of hydronium ions surrounded by an upward-moving sheath of hydroxyl ions, the resulting charge separation being supported by the charge and excluded volume of the spheres themselves [2, 4]. However, this mechanism appears not to explain all of the clusters’ features.

In particular, many colloidal vortex rings surround static free-floating colloidal crystals [6], some of which appear to be crystalline monolayers. The spheres in these
close-packed domains are not flocculated, and disperse immediately once the driving field is turned off. The crystals’ formation and stability suggests that each cluster has a stagnation plane along its midplane, quite unlike a conventional vortex ring.

Individual clusters sometimes develop breathing-mode instabilities with periods of a few seconds. Figure 1(f) tracks the evolution of an oscillating cluster’s radius of gyration, $R_g$, measured from images such as Figs. 1(b) – (e). Remarkably, the cluster’s crystalline core is destroyed and reformed with each cycle. Neighboring clusters’ oscillations do not become phase locked, and steadily circulating clusters can coexist with oscillating clusters. Consequently, distortions in the ionic fluxes entrained by a cluster appear to be well localized.

Clusters drift freely across the field of view and so cannot result from defects in the thin-film electrodes. Less dense polystyrene sulfate and poly-(methyl methacrylate) spheres do not form rings, but rather rise directly to the upper electrode where they form interfacial crystals [1, 2], as do silica spheres smaller than roughly 2 $\mu$m in diameter. These observations demonstrate that colloidal vortex rings emerge as a cooperative phenomenon among spheres driven both by electrokinetic forces and by gravity. How these forces conspire to create hierarchically structured vortex rings is an outstanding challenge. Understanding the origin of the crystalline core could lead to new methods for creating free-floating opals of technologically relevant materials.

This research was supported by the MRSEC program of the NSF.

---