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Properties and electrokinetic behavior of non-dilute colloidal suspensions

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ABSTRACT

This paper is a critical review of how the fluid properties (e.g., density, viscosity, conductivity, and permittivity) and behaviors (e.g., electrophoretic motion, electrokinetic aggregation, chaining, and instabilities) depend on colloid volume fraction. The review focuses on electrokinetic flows in aqueous solutions with suspensions on the order of a few percent that are not considered *concentrated*, yet may exhibit several behaviors distinct from dilute systems such as non-linear dependence on the particle volume fraction and unexpected behavior such as chaining, aggregation, and instabilities. This *non-dilute* regime is applicable to a variety of emerging applications such as field induced pattern formations in colloidal dispersions, electrophoretic deposition of colloidal films, nanofluid based thermal management, micron resolution particle image velocimetry, and field induced separations in lab-on-a-chip devices. These applications are often treated as dilute when in fact they may contain considerable volume fractions of particles with significant variations in the particle mobility, fluid electrical conductivity and permittivity, as well as the fluid behavior. Original results on electric field induced particle chaining and aggregation as well as fluid instabilities that may develop due to variations in conductivity and permittivity fields are briefly presented.

1. Introduction

The transport of non-dilute colloidal suspensions under externally applied electric fields are important in a number of applications such as, electrorheology (Espin et al., 2005; Hao, 2002; Ikazaki et al., 1998), field induced pattern formations in colloidal dispersions (Lumsdon et al., 2004, 2003; Trau et al., 1995; Velev and Bhatt, 2006; Whitesides and Grzybowski, 2002), electrophoretic deposition of colloidal films (Hayward et al., 2000; Trau et al., 1996), electrokinetic bead based biosensors (Velev and Kaler, 1999), nanofluid based thermal management (Jang and Choi, 2006), and field induced separations such as field flow fractionation and dielectrophoresis. In addition, recent work in micro and nanofluidic systems have focused on the electrokinetic injection, separation, concentration, and mixing of charged particles or analytes where significant volume fractions of charged species may be encountered locally (Bazant and Squires, 2004; Stone and Kim, 2001). Electrokinetics (EK) is a branch of electrohydrodynamics (EHD) that describes the electric field driven transport of ions, fluid flow, and particles and is distinguished from EHD by the presence of charges at the interface of the solid–liquid boundaries (Saville, 1997).

In this work we consider electrokinetic flows with colloidal suspensions at low Reynolds numbers. The volume fraction of the colloidal suspension can be defined as,

$$\phi = \frac{4}{3}\frac{\pi n a^3}{V} \tag{1}$$

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where a is the sphere radius, n is the number of spheres, and V is the volume of consideration. The number density of the spheres is simply n/V. In a microfluidic system used for biochemical analysis the suspension may be made up of a variety of biomolecules (e.g. nucleic acids and proteins), cells, or perhaps spheres or barcodes in multiplexed assays. In addition, it is common to use charged colloids for characterizing the flow field within microfluidic devices using optical diagnostic techniques such as micron resolution particle image velocimetry. In contrast, for material deposition processes such as colloidal crystal deposition the colloids may consist of charged spheres, wires, tubes, hexagons, or Janus particles.

This paper is a critical review of how the fluid properties (e.g. density, viscosity, conductivity, and permittivity) and behaviors (e.g. electrophoretic motion, electrokinetic aggregation, chaining, and instabilities) vary with *non-dilute* volume fractions. The terms *dilute* and *concentrated* are commonly used throughout the electrokinetics and rheology literature. In a recent review paper, Stickel and Powell defined ‘‘dense” or ‘‘highly concentrated” suspensions for rheological flows in three ways, including: (a) the average separation distance between the particles is equal to or smaller than the particle size, (b) multiple-body interactions as well as two-body lubrication contribute significantly to the rheology of the suspension, and (c) the rheology is non-Newtonian (Stickel and Powell, 2005). In the Measurement and Interpretation of Electrokinetic Phenomena in International Union of Pure and Applied Chemistry (IUPAC) dilute and concentrated terms are not precisely defined, but propose that,

> .... electrophoresis can help in making a distinction between concentrated and dilute systems by studying the dependence of the electrophoretic mobility on the concentration of dispersed particles. If there is no dependence, the behavior is that of a dilute system (Delgado et al., 2005, 2007).

Typically, a concentrated suspension in the electrokinetics literature may have volume fractions of greater than 10% (Ahualli et al., 2006; Carrique et al., 2001, 2002, 2003a,b, 2007, 2006; Cuquejo et al., 2006; Ding and Keh, 2001; Dukhin et al., 1999; Johnson and Davis, 1999; Lee et al., 2001; Midmore and Obrien, 1988; Mizuno et al., 2000; Mooney, 1951; Ohshima, 1999, 2000; Perez and Lemaire, 2004; Zukoski and Saville, 1987, 1989). It is common place to present the incremental change in a fluid or particle property (e.g. conductivity, permittivity, or mobility) in units normalized by the volume fraction. This formulation suggests that the property varies linearly with the volume fraction such that simple multiplication will result in the physical change in the property of interest. If the property varies non-linearly with the volume fraction this normalization is no longer useful. Here we are interested in electrokinetic flows with suspensions on the order of a few percent that are not considered *concentrated*, yet they may have non-linear dependence on the particle volume fraction; can result in unexpected behavior such as chaining, aggregation, and instabilities; and are applicable to a variety of emerging applications such as field induced pattern formations in colloidal dispersions, electrophoretic deposition of colloidal films, nanofluid based thermal management, micron resolution particle image velocimetry, and field induced separations in lab-on-a-chip devices. These applications mentioned above are often treated as dilute when in fact they can contain considerable volume fractions of particles with significant variations in the particle mobility, fluid conductivity and permittivity, as well as the fluid behavior. We consider this regime to be *non-dilute.*

Here we review variation in particle electrophoretic mobility, solution conductivity and permittivity with the particle volume fraction. We also review and present original results on electric field induced particle chaining and aggregation as well as fluid instabilities that may develop due to variations in conductivity and permittivity fields. The work presented and the papers reviewed are focused on electrolyte solutions with dielectric colloids. This regime is distinct from electrorheological suspensions that consist of an insulating liquid medium embodying either a semi-conductive particulate material or a semi-conductive liquid material usually a liquid crystal material (Hao, 2002).

2. Variation in fluid properties

The presence of colloids in solution can modify the suspension properties. Here we specifically interested in the electrokinetic properties such as the particle mobility as well as the suspension properties such as the electrical conductivity and permittivity. We also briefly review the variation of the fluid viscosity.

2.1. Variation of solution viscosity

The bulk viscosity varies with the colloidal volume fraction. Numerous experimental and theoretical investigations have been carried out to relate the viscosity of colloidal suspensions with the volume fraction of particles. One of the first relations of suspension viscosity with the volume fraction was proposed by Einstein in 1906. He suggested that for a collection of hard spherical particles whose radii is larger than those of the solvent, and assuming no slip at the solid–liquid boundary, creep flow and no particle hydrodynamic interaction, the dynamic viscosity of the suspension η_s is given by the relation $\eta_s/\eta_m = (1 + 2.5\phi)$, where η_m denotes the dynamic viscosity of the solvent medium. Einstein’s relation has been extensively subjected to experimental verification and proved to be accurate within a few percent for $\phi \leqslant 0.01$. For higher volume fractions of spherical particles, a number of extensions to Einstein’s equations have been proposed (Batchelor, 1977; de Kruif et al., 1986; Guth and Gold, 1938; Krieger and Dougherty, 1959; Mooney, 1951; Simha, 1940; Vand, 1948). Lyklema (2005) reviews these definitions. Colloidal suspensions at larger volume fractions such as colloidal gels and glasses can result