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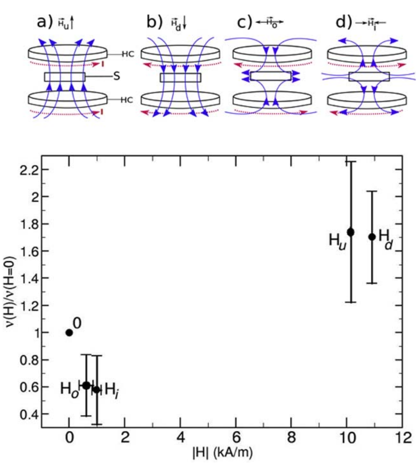
Spin-coating of moderately concentrated superparamagnetic colloids in different magnetic field configurations

Raheema Aslam[a,*], Wenceslao González-Viñas[a,b]

[a] Universidad de Navarra, Complex Systems Group, Pamplona, Spain
[b] Universidad de Navarra, PHYSMED Group, Pamplona, Spain

GRAPHICAL ABSTRACT



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ABSTRACT

Spin-coating technique is very fast, cheap, reproducible, simple and needs less material to fabricate films of particulate systems/colloids. Their thickness and uniformity may be controlled by means of external fields. We apply magnetic fields during the spin-coating of a moderately concentrated superparamagnetic colloid (made of silica coated magnetite particles). We study the influence of different magnetic field configurations (homogeneous and inhomogeneous) on the resulting spin-coated deposits and compare experimental results under various conditions. Superparamagnetic colloids behave as, non-Newtonian, magnetorheological fluids. Their viscosity vary significantly under applied magnetic fields. We measure and compare the effect of uniform and non-uniform magnetic fields on their relative effective viscosity, using the spin-coated deposits and a previously existing model for simple colloids. The mechanisms involved in the deposits formation under different experimental conditions are also discussed. In particular, we show that the magnetophoretic effect plays an important role in the spin-coating of magnetic colloids subjected to non-uniform magnetic fields. We characterize an effective magnetoviscosity in non-uniform magnetic fields that is largely influenced by the magnetophoretic effect that enhances the flow of the magnetic fluid.

* Corresponding author.
E-mail addresses: rmuhammad@alumni.unav.es (R. Aslam), wens@unav.es (W. González-Viñas).

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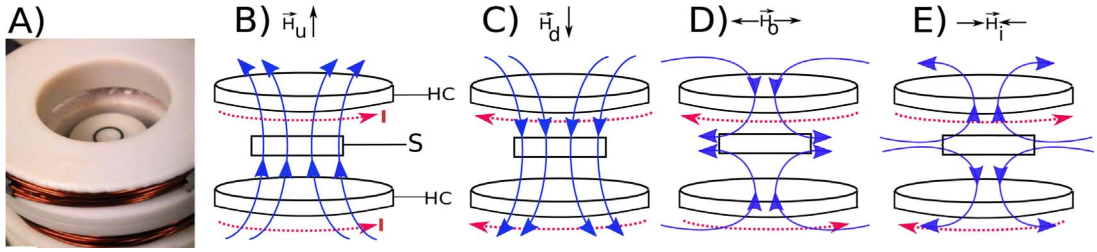

Fig. 1. (A) Photograph of spin-coater including a pair of Helmholtz coils. Reproduced from [24] with permission from the Royal Society of Chemistry. (B–D) Sketches of experimental setup configurations with magnetic field lines (HC: Helmholtz coils; S: Substrate, I: Electrical current). The substrate spins in the region of uniform magnetic field (B and C) and nonuniform magnetic fields (D and E).

1. Introduction

Spin-coating technique has been introduced in colloids to fabricate thin films and colloidal crystals since long [1–14]. It is simple, reproducible and requires little material to get results in a very short time [15]. The thickness and uniformity of spin-coated films which are important parameters for their technological applications, depend on experimental conditions including; the spin time and speed, the viscosity of fluids, the density and the evaporation rate of the fluids, concentration of the suspension and the substrate surface characteristics. The flow behavior as a function of the fluid properties in spin-coating process helps to recognize its strong performance in applications and has been investigated by many research groups through different models and experiments [2,3,5,16–21]. Spin-coating of nano-colloids has been thoroughly explored in the literature for almost a century [1]. However, for colloids of bigger particles, external fields have been used recently for tunning their effect which is not yet fully understood [22–25].

The rheological effects of magnetic fields on magnetic fluids have been studied from mid-twentieth century [26–28]. One of the most important result is that the viscosity of a magnetic fluid increases monotonously on applying a magnetic field, until it reaches a saturation value.

Superparamagnetic particles of typical size ranging from 100 nm to a few micrometers are prepared by inserting magnetic nanoparticles in a matrix of non-magnetic material (polystyrene or silica). They show a quasi-zero remanent magnetization and high magnetic response [29]. They have many interesting applications in the biomedical field, e.g. drug delivery; to deliver medicines to arteries and veins in the circulatory system of the body, due to their high magnetic response [30]. To use them for this kind of applications, superparamagnetic colloids are first functionalized to capture their specific targets. Then, magnetic gradient is applied for removing them from their targets through magnetophoresis [31]. Where, magnetophoresis defines the motion of magnetic particles in a magnetic gradient. An magnetic field results in the formation of superparamagnetic particles chains along the magnetic field which enhances the process of separation [32]. As the homogeneous magnetic fields can not induce a drift velocity in magnetic particles therefore a magnetic gradient is required for having magnetophoresis [29].

The effect of homogeneous external magnetic fields on the behavior of diluted simple superparamagnetic [22] as well as hybrid ferromagnetic [25] colloids in spin-coating have been studied. They observed an increase in the solid deposits on the substrate with applied magnetic field as compared to the sparse structures deposits obtained without applying magnetic fields. Later, they measured the magnetoviscosity of colloids from the amount of spin-coated deposits obtained without and with homegeneous magnetic fields [24,25], by generalizing a continuum model [20] to particulate systems. In summary, they proved that external uniform magnetic fields only affect the magnetoviscosity (an increase in the viscosity when a magnetic field is applied [27]) of magnetic colloids, and that the generalized model holds for diluted magnetic colloids.

In this article, we use the same previously proved generalized model for colloids [24,25], to measure the magnetoviscosity as a function of different magnetic field configurations in spin-coating. Here, moderately concentrated suspension of superparamagnetic particles in a volatile solvent is used. We measure the surface coverage of the dried deposits obtained without, with uniform and with non-uniform magnetic fields that are applied during the spin-coating of the suspension. Firstly, the experimental setup and methods are described. After, the previously existing models [20,24,25] for simple fluids and colloids are highlighted. Finally, the results obtained through spin-coating at various experimental conditions are presented and discussed. Our results corroborate that spin-coating technique allows to study magnetorheology in a very short time using a uniform magnetic field, and that the increase in effective viscosity of the colloids is the only effect of the applied magnetic field [24,25]. However, when the magnetic field is not uniform, there are other relevant effects, namely magnetophoretic effect, which leads to a decrease of the effective viscosity.

2. Experimental methods

Experiments are performed in a customized commercial spin-coater (Laurell technologies, WS-650SZ-6NPP/LITE/OND) at rotation rate of 2000 rpm. The photograph of the spin-coater provided with Helmholtz coils is shown in Fig. 1A. Sketches of the experimental setup evidencing applied magnetic field of various configurations obtained by a pair of Helmholtz coils which are placed in such a way that the substrate spins in the region of uniform axial (Fig. 1B and C) and nonuniform fields (Fig. 1D and E). Different applied magnetic field configurations are generated by adjusting the orientation of a fixed electrical current (5 A) in these coils with an external power supply. Using this experimental setup we obtain four different configurations of the magnetic field which are detailed in Table 1.

Superparamagnetic particles obtained from microParticles GmbH, Germany, that consist of silica coated magnetite of diameter $1.51 \pm 0.05\,\mu m$ (density = 1.6–1.8 g/cm^3), are used for all experiments. Their magnetic properties can be found in the Electronic Supplementary Information of [24]. The particles are dried overnight and then weighted for preparing suspension of concentration of 12.82%(v/v) in Methyl Ethyl Ketone (MEK). The estimated dynamic viscosity of the colloid (at zero-field) is 55% bigger than the one of the solvent alone [33]. The suspension is ultrasonicated for fifteen minutes before each experiment. The spin-coater is operated at 2000 rpm and the magnetic field H is applied. Then, 100 µl of suspension is pipetted onto the spinning substrate. Once the spun suspension is dried, the field is turned off. Images of the dried deposits on the substrates are taken with a white light reflection microscope at 2 mm intervals from the center of spinning. After, we analyzed one micrograph for each set (H, r), where r is the distance from the center of spinning.

For all experiments, glass substrates of an approximate size of $38 \times 25 \times 1\,mm^3$ are used. First, they are cleaned in soft basic piranha for forty minutes at 67 °C (piranha is a mixture of ultra-pure water/ammonia/

Table 1
Various magnetic field configurations, their symbols and magnitudes, used for performing spin-coating experiments.

Configuration	Symbol	Magnetic field (|H|) [kA/m]
Zero-field	0	0
Up	H_u	10.145 ± 0.005
Down	H_d	10.915 ± 0.005
Outward	H_o	0.61 ± 0.26
Inward	H_i	0.99 ± 0.16