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Wetting of ferrofluids: Phenomena and control

Mika Latikka [a,*], Matilda Backholm [a], Jaakko V.I. Timonen [a], Robin H.A. Ras [a,b]

Ferrofluids are liquids exhibiting remarkably strong response to magnetic fields, which leads to fascinating properties useful in various applications. Understanding the wetting properties and spreading of ferrofluids is important for their use in microfluidics and magnetic actuation. However, this is challenging as magnetically induced deformation of the ferrofluid surface can affect contact angles, which are commonly used to characterize wetting properties in other systems. In addition, interaction of the magnetic nanoparticles and solid surface at nanoscale can have surprising effects on ferrofluid spreading. In this review we discuss these issues with focus on interpretation of ferrofluid contact angles. We review recent literature examining ferrofluid wetting phenomena and outline novel wetting related ferrofluid applications. To better understand wetting of ferrofluids, more careful experimental work is needed.

Address
[a] Department of Applied Physics, Aalto University School of Science, P.O. Box 15100, FI-00076 Aalto, Espoo, Finland
[b] Department of Bioproducts and Biosystems, Aalto University School of Chemical Engineering, P.O. Box 16100, FI-00076 Aalto, Espoo, Finland

[*] Corresponding author.
(mika.latikka@aalto.fi)

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1. Introduction

Ferrofluids are colloidal suspensions of small (~3–15 nm diameter [1]) superparamagnetic nanoparticles in a liquid carrier medium. They combine liquid properties with a strong magnetic response, and thus exhibit fascinating phenomena, such as field-induced pattern formation on the ferrofluid surface [2], self-assembly of droplets [3] and magnetic micro-convection [4] (Fig 1). The superparamagnetic nanoparticles used in ferrofluids usually consist of ferri- or ferromagnetic metals or metal oxides [5•]. Due to the small nanoparticle size, Brownian motion is enough to keep the particles from settling in gravitational or magnetic fields [2]. The small size also renders the nanoparticles superparamagnetic: each particle acts as a single magnetic domain (although surface effects and structural defects can influence this [6]), which can flip its magnetization direction due to thermal agitation. Due to this Neél relaxation together with rotational Brownian relaxation, ferrofluids show no remanent magnetization in room temperature once the external magnetic field is removed [5•]. This lack of magnetic hysteresis is also exhibited by paramagnetic materials, but otherwise superparamagnetic particles resemble ferri- or ferromagnetic materials with high susceptibility and nonlinear response to magnetic fields [1].

Superparamagnetic nanoparticles can be fabricated using either a top-down approach, such as grinding of larger particles [7], or a bottom-up approach, i.e. chemical synthesis. The latter is nowadays more widely used, especially chemical co-precipitation involving Fe^{3+} and Fe^{2+} salts in water [5•], [8]. To prevent aggregation caused by attractive forces between the particles, such as van der Waals and magnetic dipole interactions [9], the nanoparticles need to be stabilized. This is done by introducing interparticle repulsion by charging the particles (electrostatic stabilization) or by coating them with capping agents (steric stabilization) [5•]. These capping agents are usually

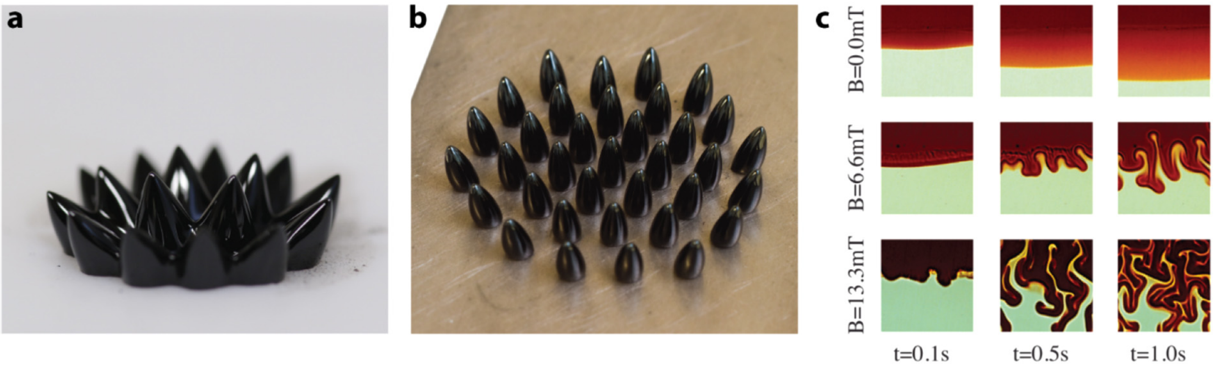

Fig. 1 Phenomena exhibited by ferrofluids under magnetic field. a) Field-induced surface pattern formation. b) Self-assembly of ferrofluid droplets on a superhydrophobic surface. c) Snapshots of micro-convective mixing of ferrofluid and water in a microfluidics channel in different magnetic flux densities *B*. c) adapted from [4] with permission from Elsevier.

surfactants, especially in case of ferrofluids with organic carrier liquid. For a more thorough introduction to the properties of ferrofluids we direct the reader to an excellent recent review by Torres-Díaz and Rinaldi [10••].

Stable, magnetically controllable liquids are useful in a range of mechanical to biomedical applications. Ferrofluids are widely used as liquid seals and lubricants held in place by magnetic fields, while actuation with dynamic magnetic fields allow building of ferrofluid based pumps, valves and tunable optical systems [5•,10••]. Their anisotropic heat transfer capabilities find use as heat transfer fluids and magnetic buoyancy can be exploited in separation processes [5•,10••]. Recently ferrofluids have been increasingly investigated for microfluidic [11•–13•] and biomedical [14•] applications. In many of these cases, the ferrofluid wetting properties need to be carefully understood and tuned in order to ensure reliable function of these systems. In this review we discuss the wetting properties of ferrofluids, how they can be controlled with external magnetic fields and some interesting applications from the past few years.

2. Wetting of ferrofluids

2.1. Contact angles

Wetting characterization relies heavily on the concept of contact angle, which is the angle between the solid-liquid and liquid-air interfaces [15•]. The smaller the angle, the better the liquid wets the surface. The contact angle value typically depends on the length scale it is measured on (Fig 2a-c) [16–19]. The microscopic, actual contact angle existing locally at each point on the contact line would be the ideal quantity for measuring wetting properties, but it is unfortunately very difficult to probe experimentally (Fig 2b). Usually a macroscopic apparent contact angle (measured at length scales over tens of micrometres) is used instead, which represents an average value of the microscopic local contact angles (Fig 2a). Care must be taken when measuring the apparent contact angle, because body forces (for example gravity) not related to wetting properties can deform the droplet profile. Because of this, the apparent contact angle must be determined using appropriate magnification. Finally, all three phases (solid, liquid and gas) are very close to one another near the contact line at the nanoscale. This gives rise to a disjoining pressure, which determines the curvature of the liquid surface near (<100 nm) the solid surface (Fig 2c) [16–18]. The exact surface geometry is again difficult to probe experimentally due to the small scale.

The apparent contact angle can be interpreted to reflect the average molecular wetting properties, that is the interfacial tensions between solid, liquid and surrounding fluid (immiscible liquid or gas), which is why it is used for wetting characterization. This angle is rarely unique, but can instead have a range of metastable values, for example

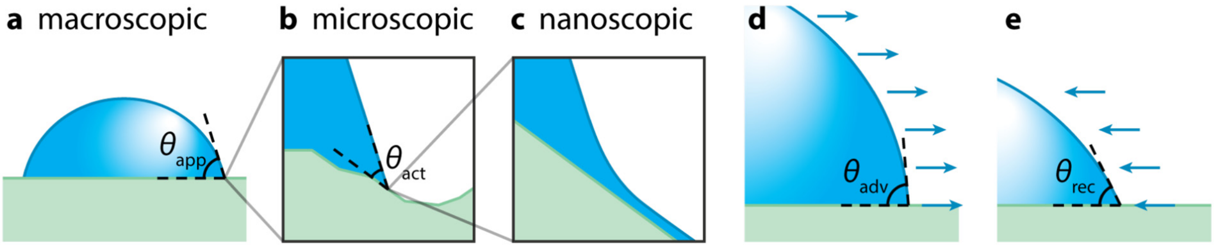

Fig. 2 Contact angles in wetting characterization. a) Apparent contact angle at the macroscale. b) Actual contact angle at the microscale. c) Transition to a thin film at the nanoscale due to disjoining pressure. d) Advancing contact angle. e) Receding contact angle.