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Investigations on the magnetization behavior of magnetic composite particles

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ABSTRACT

In life sciences the application of surface functionalized magnetic composite particles is establishing in diagnostics and in downstream processing of modern biotechnology. These magnetic composite particles consist of non-magnetic material, e.g. polystyrene, which serves as a matrix for the second magnetic component, usually colloidal magnetite. Because of the multitude of magnetic cores these magnetic beads show a complex magnetization behavior which cannot be described with the available approaches for homogeneous magnetic material. Therefore, in this work a new model for the magnetization behavior of magnetic composite particles is developed. By introducing an effective magnetization and considering an overall demagnetization factor the deviation of the demagnetization of homogeneously magnetized particles is taken into account. Calculated and experimental results show a good agreement which allows for the verification of the adapted model of particle magnetization. Besides, a newly developed magnetic analyzing centrifuge is used for the characterization of magnetic composite particle systems. The experimental results, also used for the model verification, give both, information about the magnetic properties and the interaction behavior of particle systems. By adding further components to the particle solution, such as salts or proteins, industrial relevant systems can be reconstructed. The analyzing tool can be used to adapt industrial processes without time-consuming preliminary tests with large samples in the process equipments.
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1. Introduction

Nanoscale magnetic particles have a wide range of applications from information technology and machine construction up to medical technology and selective separation.

In life sciences the application of surface functionalized magnetic composite particles is establishing in diagnostics. The particles have a size of several μm allowing for a better applicability and processability. Pure magnetite particles of that size consist of thousands of magnetic domains and are not superparamagnetic. To maintain the advantageous superparamagnetic character, magnetic composite particles consist of different materials instead. The first is a non-magnetic material, e.g. polystyrene, which serves as a matrix for the second magnetic component, usually colloidal magnetite. The magnetite particles which are incorporated into the matrix have a mean diameter smaller than 20 nm, creating a superparamagnetic character of the whole particle. Besides better handling the polymeric matrix with functional surface groups enables a grafting of ligands, which allows selective interactions with molecules according to the key-lock-principle. That allows to selectively identify and separate specific types of DNA, proteins, enzymes (e.g. hydrogenases, trypsin), monoclonal antibodies or other molecules [10,20,21]. Also in the emerging field of modern biotechnology in downstream processing the use of these magnetic beads with their functionalized surfaces to separate target bio products like protein or enzymes from bio broth by selective adsorption is investigated to be implemented in industrial production processes, e.g. lysozyme or soy protein separation [8,15].

In such separation processes the interplay of magnetic and other forces are important to control and direct the particle movement. Depending on the magnitude of the acting magnetic force it can influence the whole separation process by specific movement or magnetically induced agglomeration of the magnetic particles. Especially in the sector of downstream processing there is a need for fast test methods to characterize the bulk behavior of the magnetic beads and the impact of the process fluids on the particle interaction.

Most magnetic separation methods work discontinuously to remove collected magnetic particles without the magnetic field being active. Lindner reports of the development of a centrifugal

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high gradient magnetic filter which is based on the principle of removing collected magnetic particles continuously without removing the collecting matrix out of the magnetic field. In this case the centrifugal force must be strong enough to overcome the magnetic force, which is applied for collecting the magnetic particles [15].

In this work a magnetic analytical centrifuge is presented, which is suitable to characterize the magnetic behavior of particulate systems by applying magnetic and centrifugal forces at the same time. Depending on the properties and the surrounding process fluid the superposed magnetic field influences the particle aggregation and movement in the centrifugal field. For example for the separation device presented by Lindner the magnetic analytical centrifuge could provide a feasible and quick method to determine the necessary centrifugal force to remove the magnetic particles out of the acting magnetic field. This way, the working point for the industrial separation unit could be determined easily.

Agglomeration processes due to magnetic interactions have already been intensively studied for ferrofluids [4,11,19]. The agglomeration occurs due to the reduction of the magneto static energy in the overall system. Attractive forces in the direction of the external field and repulsive forces perpendicular to the magnetic field lead to the formation of an agglomeration of chain-like structures [5,6]. For strong interactions particles align as thin, long chains with only single particles in diameter. This is due to the stronger influence of the repulsive potential between the particles perpendicular to the magnetic field [22]. Paranjpe and Elrod calculate the maximum chain length by minimizing the potential energy of agglomerates. At the same time they examine the stability of these chains by allowing small displacements from the stable state and study the resulting forces acting on the particles within the agglomerate [18].

Only very few methods exist to describe the magnetic behavior of composite particles. Typically the magnetization properties are averaged over the whole particle volume to employ principles used for homogeneous particles. However, this leads to erroneous results, since additional effects e.g. intrinsic demagnetization must be taken into account at the microscopic level. Although, some approaches exist to calculate the susceptibility and the demagnetization factor [2,3,13] of such particles no suitable approach for the interparticle magnetic dipole interactions exists, which considers these parameters. Thus, to identify the order of magnitude of the dipole interactions a magnetization model based on an effective magnetization linked with the demagnetization factor is developed. A comparison of calculated and experimental results confirms the model for composite particles. The same model was already applied in a discrete element method simulation (DEM) of the magnetic cake filtration of composite particles [7].

2. Theory

2.1. Magnetism

The magnetization M of an isotropic material within a homogenous magnetic field is proportional to the field strength H_0 and the susceptibility χ of the material. The susceptibility depends on the material but also on the form. Form-independent characteristics can be determined on ring-shaped samples [9]; the susceptibility then is known as the intrinsic susceptibility. The reason for the dependence of the particle shape lies in the pattern of the magnetic field strength H_i inside the material. Its direction is opposite to the external field strength. Depending on the magnetization M and demagnetization factor D_M the weakening of the local field strength is given by

$$H_i = H_0 - D_M \times M. \tag{1}$$

If the demagnetization factor D_M and the intrinsic susceptibility χ_i are known, then it is possible to calculate the shape-dependent susceptibility of a sample

$$\chi = \frac{\chi_i}{1 + D_M \times \chi_i}. \tag{2}$$

A threshold analysis can be done for low and for high field strengths. In the first case χ_i is very high and gives the approximation $\chi \approx D_M^{-1}$. In the case of high field strengths well above saturation magnetization χ_i is small resulting in the correlation $\chi \approx \chi_i$ [9]. In the case of higher field strengths, susceptibility loses its dependence on particle shape.

The demagnetization factor D_M mainly depends on the sample shape and direction of magnetization, with the range $0 < D_M < 1$. Spheroids behave isotropic and $D_M = 1/3$ in each direction. For more complex geometries calculated values are only of limited value [26]. If the direction of magnetization deviates from the longitudinal axis of the sample, i.e. the preferred direction, then the D_M increases due to the increasing shape anisotropy.

2.2. Composite particles

Composite particles consist of two or more components, whereof one has a matrix function. The other components are incorporated. The materials preserve their physical properties and do not interact chemically. The properties of the composite depend on their relative distribution in the matrix and

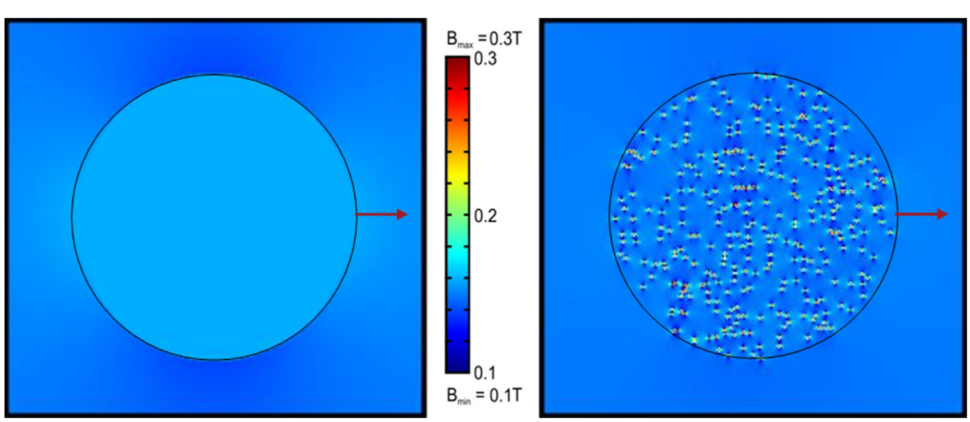

Fig. 1. False color representation of the magnetic flux density in the vicinity of a magnetized homogenous magnetic particle (left) and a composite particle (right) computed in 2D using COMSOL: Material parameters: diameter of the particle $d_0 = 40$ mm; diameter of a magnetite core within the particle (right) $d_{core} = 0.4$ mm; mass fraction of magnetite $x_m = 0.04$; $B_0 = 0.148$ T; $\chi_{homogenous} = 0.176$; $\chi_{core} = 4.41$.

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