

micromod Partikeltechnologie GmbH

modular designed particles



Technological Applications

Publications and Reviews

magnetic micro- and nanoparticles

Implementation in Life Sciences

www.micromod.de

Product overview

	10 nm	100 nm	1 µm	10 µm	100 µm	Product matrix
Magnetic particles	20 nm – 500 nm					dextran
		80 nm – 100 nm				bionized nanoferrite
			2 - 12 µm			polystyrene
				30 µm - 100 µm		poly(lactic acid)
		350 nm - 6 µm				silica
		150 nm				poly(ethylene imine)
		150 nm				chitosan
		50 - 250 nm				iron oxide
Fluorescent particles	10 nm – 20 µm					silica
	25 nm		6 µm			polystyrene, polymethacrylate
		250 nm		100 µm		poly(lactic acid)
Fluorescent magnetic particles		250 nm				albumin
		100 nm - 300 nm				dextran
		100 nm		30 µm - 100 µm		bionized nanoferrite poly(lactic acid)
White particles	10 nm – 20 µm					silica
	25 nm			100 µm		polystyrene, polymethacrylate
		250 nm		100 µm		poly(lactic acid)
		300 nm				latex
		250 nm				albumin
Colored particles		100 nm		100 µm		silica
			1 µm - 12 µm			polystyrene
		250 nm		100 µm		poly(lactic acid)
	10 nm	100 nm	1 µm	10 µm	100 µm	

micromod Partikeltechnologie GmbH
Friedrich-Barnewitz-Straße 4, D-18119 Rostock
Tel.: +49 381/54 34 56 10, Fax: +49 381/54 34 56 20
Technical Support Tel.: +49 381/54 34 56 14
E-mail: info@micromod.de, Internet: www.micromod.de

3 Terminology and characteristics of magnetic nanoparticles

Kerstin Witte^{1,2}, Fritz Westphal²

¹ University of Rostock, Institute of Physics, Albert-Einstein-Str. 23, 18059 Rostock, Germany

² micromod Partikeltechnologie GmbH, Friedrich-Barnewitz-Str. 4, 18119 Rostock, Germany

3.1 Classification of magnetic materials

If a material is placed in an external magnetic field \mathbf{H} , the individual magnetic moments of each atom will contribute to the overall magnetic induction \mathbf{B} :

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}), \quad (1)$$

where μ_0 is the vacuum permeability and \mathbf{M} the magnetization. All materials show some kind of magnetic behavior which essentially depends on the atomic structure and the temperature of the material. The magnetic behavior can be classified using the magnetic susceptibility χ :

$$\mathbf{M} = \chi\mathbf{H}. \quad (2)$$

Eq. (1) describes the magnetization which is induced by the external magnetic field. For diamagnets χ is negative and in the range of -10^{-3} up to -10^{-6} [1]. Diamagnetic behavior is present in every material, but can only be observed when no other magnetic behavior is present [2]. Most materials show small positive response in the presence of an external magnetic field. These materials are called paramagnets and their susceptibility is in the order of 10^{-6} up to 10^{-1} [1]. Here each atom in the materials has a small randomly oriented magnetic moment and the interactions between the magnetic moments are negligible. When an external field is applied the magnetic moments start to align, thus a net magnetization proportional to the external magnetic field can be observed.

Some materials also show ordered magnetic states at certain temperatures. Here, three different classes of materials can be distinguished – ferromagnets, ferrimagnets and antiferromagnets. In ferromagnetic materials the magnetic moments of each atom strongly interact with the neighboring magnetic moments leading to a parallel alignment of the moments [2]. The magnetic moments are spontaneously magnetized in regions of uniform magnetization so called domains. The response of such a ferromagnetic material is nonlinear and a hysteresis can be observed. The schematic of a hysteresis is presented in Fig. 1. After the initial magnetization of the ferromagnet in an external field the saturation magnetization M_s is reached. This magnetization corresponds to a complete alignment of the domains along the external

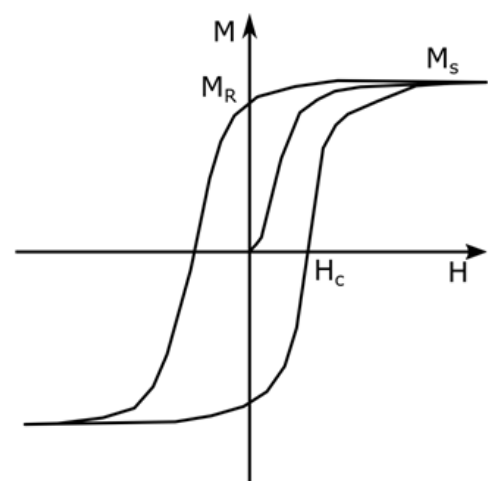


Fig. 1: Schematics of the initial magnetization curve and the hysteresis loop of a ferromagnet with main points of interest

magnetic micro- and nanoparticles

magnetic field. If the external magnetic field is reduced to zero after a first saturation of the sample, the magnetization does not reduce to zero. The magnetization left without an external magnetic field is the remanence M_R . If the magnetic field is reversed, the magnetization will further decrease and reach zero again. The magnetic field at this point is called coercivity H_C [2]. In antiferromagnetic materials the interaction between neighboring atoms is strongly negative. This leads to an antiparallel alignment of the neighboring magnetic moments. Furthermore only one kind of magnetic moment is present in the material, wherefore the antiparallel alignment of the moments leads to a net magnetic moment of zero [2]. Ferrimagnetism is normally observed in materials with two or more different species of magnetic moments. The interaction between neighboring atoms is also strongly negative, but in contrast to the antiferromagnets the magnetic moments of the atoms do not cancel out completely [2].

3.2 Magnetic anisotropy, domain structure and superparamagnetism

Ferro- and ferrimagnetic materials show certain crystallographic directions which are easier to magnetize than others. These directions are the so called easy axes of magnetization and are defined by the magnetic anisotropy. Furthermore, the magnetic anisotropy is the actual origin of hysteresis and coercivity [3]. The magnetocrystalline anisotropy involves the electrostatic crystal-field interaction and relativistic spin-orbit-coupling [3]. Considering defect free bulk materials magnetic properties as the saturation magnetization, coercivity or the Curie temperature depend only on the chemical and crystallographic structure of the material due to the magnetocrystalline anisotropy [4]. The size and shape of these materials are not crucially important.

Nanostructured magnetic materials show a wide range of unusual magnetic properties which are strongly influenced by finite size and surface effects [4]. A lot of these effects are strongly influenced by the effective anisotropy of the material. Due to the reduction of the size the influence of shape- and surface anisotropy increases and can affect the physical properties of the material and the domain structure. By reducing the particle size of a material also the number of domains will reduce. Normally a magnet consists of several domains separated by domain

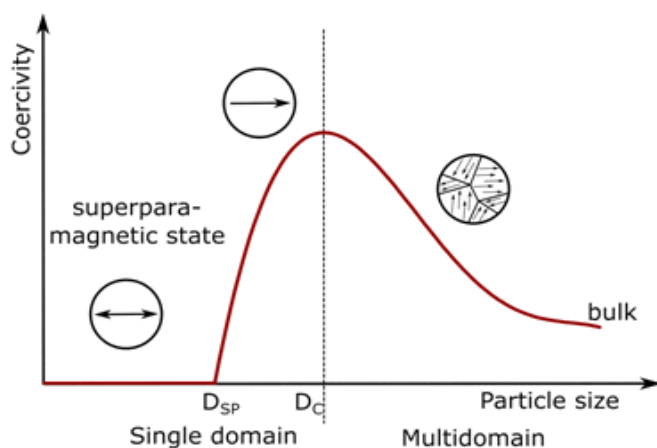


Fig. 2: Illustration of the particle size dependence of the coercivity.

walls. When the particle size is reduced these domains start to rearrange. An example for influence of the domain structure on the macroscopic properties is the behavior of the coercivity in dependence of the particle size (Fig. 2). With a decreasing particle size, the coercivity of immobilized particles increases. A maximum is reached at the certain critical size D_C . This critical size strongly depends on the effective anisotropy of the material investigated. At this size it is energetically unfavorable for

the magnet to build several domains. The magnet is in single domain state. With a further decrease of the particle size the coercivity decreases drastically and reaches zero in the superparamagnetic state [5].

Nanoparticles in a single domain state can be described by assuming that they exhibit an effectively uniaxial anisotropy with only one anisotropy constant, since the particles are so small, that all spins are aligned parallel [3]. The anisotropy energy can be described by:

$$E = K_1 V \sin 2\theta, \quad (3)$$

with K_1 being the first anisotropy constant along an easy axis, V the particle volume and θ the angle between the easy axis of magnetization and the magnetization vector. Eq. (3) shows that the anisotropy energy directly depends on the volume of the particle. When the particle size decreases, the anisotropy energy can reach the same order of magnitude as the thermal energy $k_B T$. Due to this fact flips between the energetic minima of differently oriented easy axes are possible and the nanoparticle behaves like a paramagnetic material. The time scale of such jump can be described by the Néel relaxation time, which is an exponential function:

$$\tau_N = \tau_0 e^{K_1 V / (k_B T)}, \quad (4)$$

with τ_0 being the Néel relaxation constant in the order of 10^{-9} s [6]. It describes the time constant necessary for a particle to relax into an energetic minimum after a perturbation. When the Néel relaxation time of a nanoparticle is in the same order of magnitude as the measurement time, the superparamagnetic effect is observed. This measurement time can be different for different measurement methods and the transition to the superparamagnetic state can be observed for different particle sizes.

3.3 Relaxation behavior und frequency dependent susceptibility

Considering non-immobilized magnetic nanoparticles in suspension two relaxation mechanisms can be observed – Néel and Brown relaxation. The Néel relaxation as described above is a rotation of the magnetic moments within the particles. Brown relaxation is originated by a diffusive rotation of the particles in the liquid [7]. The Brownian relaxation can be described with the Brownian relaxation time τ_B by:

$$\tau_B = \frac{\pi \eta d_h^3}{2 k_B T}, \quad (5)$$

with η being the viscosity of the solution and d_h the hydrodynamic diameter of the particles [7, 8]. It is to be seen that in both cases, for Néel as well as for Brown relaxation, the relaxation time depends on the particle volume. Since both relaxation mechanisms are possible in a particle suspension, an effective relaxation time τ_{eff} as a linear combination of both relaxation processes can be observed [8]

$$\tau_{\text{eff}} = \frac{\tau_N \tau_B}{\tau_N + \tau_B} \quad (6)$$

The relaxation behaviour of nanoparticles with different diameters is dominated by different

relaxation mechanisms. When the Néel relaxation time is significantly longer than the Brownian relaxation time, the particles are in the so called blocked state [9].

In Eq. (2) a simple relation between the magnetic field and the magnetization was introduced via the susceptibility. Considering small amplitudes of the external field the susceptibility can be described independent from the external magnetic field [7]. The irreversibility of the hysteresis is taken into account when the susceptibility is described to be complex [7]. Therefore, in an alternating magnetic field the magnetic susceptibility can be described by:

$$M = \chi H = (\chi' - i\chi'')H, \quad (7)$$

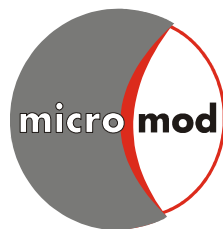
where χ' is the real and χ'' the imaginary part of the susceptibility. According to the Debye model the complex susceptibility in dependence on the applied frequency can be described by [10]:

$$\chi(\omega) = \frac{\chi_0}{1 + i\omega\tau_{\text{eff}}} \quad (8)$$

However, ensembles of magnetic nanoparticles normally exhibit a distribution of relaxation times due to particle size distribution and are usually described by a log-normal distribution of the effective relaxation time.

References

- [1] Pankhurst, Q.A., et al., *Applications of magnetic nanoparticles in biomedicine*. Journal of physics D: Applied physics, 2003. **36**(13): p. R167.
- [2] Krishnan, K.M., *Fundamentals and applications of magnetic materials*. 2016: Oxford University Press.
- [3] Skomski, R., *Simple models of magnetism*. 2008: Oxford University Press on Demand.
- [4] Gubin, S.P., *Magnetic nanoparticles*. 2009: John Wiley & Sons.
- [5] Bean, C. and J. Livingston, *Superparamagnetism*. Journal of Applied Physics, 1959. **30**(4): p. S120-S129.
- [6] Néel, L., *Influence des fluctuations thermiques sur l'aimantation de grains ferromagnétiques très fins*. Comptes rendus hebdomadaires des séances de l'Académie, 1949. **228**(8): p. 664-666.
- [7] Hergt, R., S. Dutz, and M. Zeisberger, *Validity limits of the Néel relaxation model of magnetic nanoparticles for hyperthermia*. Nanotechnology, 2009. **21**(1): p. 015706.
- [8] Astalan, A.P., et al., *Biomolecular reactions studied using changes in Brownian rotation dynamics of magnetic particles*. Biosensors and Bioelectronics, 2004. **19**(8): p. 945-951.
- [9] Astalan, A.P., et al., *Magnetic response of thermally blocked magnetic nanoparticles in a pulsed magnetic field*. Journal of Magnetism and Magnetic Materials, 2007. **311**(1): p. 166-170.
- [10] Debye, P., *Polar Molecules*. 1945. New York: Dover.



Editor:
micromod Partikeltechnologie GmbH

Registergericht: Amtsgericht Rostock HRB 5837
Steuernummer: 4079/114/03352
Ust-Id Nr. (Vat No.): DE167349493

Compilation date - May the 10th, 2017
micromod Partikeltechnologie GmbH