

## Colloidal stability in magnetic fluids: effects of the intrinsic dipolar magnetic field in magnetic semiconductors

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2008 J. Phys.: Condens. Matter 20 204114

(<http://iopscience.iop.org/0953-8984/20/20/204114>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 29/05/2010 at 12:00

Please note that [terms and conditions apply](#).

# Colloidal stability in magnetic fluids: effects of the intrinsic dipolar magnetic field in magnetic semiconductors

Fanyao Qu<sup>1</sup>, D R Santos Jr<sup>2</sup> and P C Morais<sup>3</sup>

<sup>1</sup> Universidade Federal de Uberlândia, Instituto de Física, Uberlândia MG 38400-902, Brazil

<sup>2</sup> Departamento de Física, Universidade Federal de São Carlos, 13565-905, São Carlos, São Paulo, Brazil

<sup>3</sup> Universidade de Brasília, Instituto de Física, Núcleo de Física Aplicada, Brasília DF 70910-900, Brazil

E-mail: [fanyao@ufu.br](mailto:fanyao@ufu.br)

Received 1 April 2008

Published 1 May 2008

Online at [stacks.iop.org/JPhysCM/20/204114](http://stacks.iop.org/JPhysCM/20/204114)

## Abstract

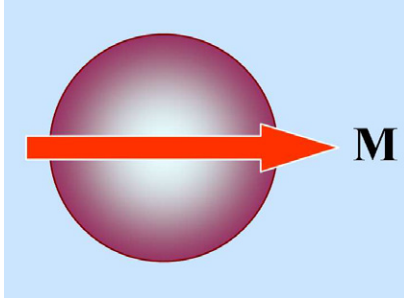
The effects of the intrinsic dipolar magnetic field on the energy levels and charge density distribution of a spherical magnetic semiconductor nanoparticle have been investigated in the framework of quantum mechanics using the finite element method. It was found that the dipolar magnetic field not only removes the degeneracy of the energy levels, resulting in a redistribution of carriers, but also directly changes the charge density distribution, leading to a modification of the surface charge density with a strong influence upon the colloidal stability. These effects strongly depend on both the nanoparticle magnetization value and the nanoparticle size. The bigger the nanoparticles, the larger the effects of the intrinsic dipolar magnetic field upon the charge density distribution.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Magnetic fluids represent a very special class of colloids in which the dispersed nanosized particles, usually metal oxide–semiconductor ones, possess permanent magnetic moments [1]. They present a variety of fascinating properties which demonstrate potential applications in spintronics, quantum information processes and medicine [2, 3]. In spite of the great experimental and theoretical efforts, however, the long term colloidal stability still remains a challenge for applications [2, 3]. Thus, any effort towards the understanding of basic aspects for further improvement of the magnetic fluid (MF) colloidal stability has a major impact on the applied research [4]. For about six decades the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory has been used as the starting point for analyzing the huge amount of experimental data related to colloids [5]. Refinements of the keystone double-layer model for the metal oxide–electrolyte interface, for instance the three-layer model [6] and the four-layer model [7], have made

an important progress in illustrating fine structures of the solid–liquid interfaces in colloidal systems. Nevertheless, neither the DLVO theory nor any of its refinements provides a first-principles-based microscopic view of the mechanism through which the nanoparticle’s charge density distribution in ionic colloids sets up, owing to the absence of a proper quantum mechanical description of the charge-transfer mechanism across the nanoparticle solid–liquid interface. The very first attempt to solve this problem was accomplished by self-consistently solving the coupled three-dimensional Schrödinger and Poisson equations in the frame of the effective-mass approximation, using the finite difference method (FDM) [8]. For the suspended MF nanoparticle the surface charge density, electronic structure and Fermi energy were studied as a function of the band offset at the solid–liquid interface [8]. The success of such formulations for spherical metal oxide nanoparticles dispersed in aqueous medium permits us to investigate the size dependence of the charge density distribution at a given pH and of band offset values [9, 10]. The influence of the nanoparticle’s deviation



**Figure 1.** Schematic diagram of the uniformly magnetized spherical nanoparticle ( $\text{Fe}_3\text{O}_4$ ) with magnetization  $\mathbf{M}$  immersed in an aqueous medium.

from the spherical shape on the charge density distribution was also reported [11–13]. Furthermore, excellent agreement [14] of the titration curves of ionic colloids, obtained from quantum mechanical models, with the experimental data available in the literature [15–17] has been achieved. Although experimental observations show that the intrinsic dipolar magnetic field associated with the magnetic nanosized particle is crucial for the stability of ionic magnetic fluids, this point has not been addressed theoretically to date, mainly due to the complicated calculation involved. In this paper, the effect of the intrinsic dipolar field upon the charge density distribution in ionic magnetic colloids is derived using the quantum mechanical viewpoint. The quantum mechanical equation involved in the problem formulation is numerically solved in the framework of finite element method (FEM) taking into account the effects of the nanoparticle size and shape [18]. This paper is organized as follows. Section 2 describes how the intrinsic dipolar field is introduced into the Schrödinger equation and how Galerkin’s weighted residue method [18] is used to obtain the finite element matrix form of this equation. Section 3 contains the main contribution of the paper: calculation of the effects of the dipolar magnetic field on the charge density distribution due to changes on the particle size and particle magnetic moment. Finally, section 4 presents our conclusions.

## 2. Theoretical model

The effect of the dipolar magnetic field on the charge density distribution of a typical spherical magnetic nanoparticle ( $\text{Fe}_3\text{O}_4$  for instance) immersed in an aqueous medium has been investigated, using a truly three-dimensional model, as shown schematically in figure 1. The spherical nanoparticle (radius  $R$ ), with uniform permanent magnetization ( $\vec{M} = M_0 \vec{z}$ ), is surrounded by low or high pH aqueous medium. The magnetization gives equivalent currents. These currents produce a constant magnetic field inside and a dipole magnetic field outside the nanoparticle. In spherical coordinates ( $r, \theta, \varphi$ ) the magnetic vector potential  $\vec{A}$  reads

$$\vec{A} = \frac{4\pi}{3} M_0 R^2 \left( \frac{r_{<}}{r_{>}^2} \right) \sin \theta \cdot \hat{e}_\varphi, \quad (1)$$

where  $r_{<}$  ( $r_{>}$ ) is the smaller (larger) of  $r$  and  $R$ , and  $\hat{e}_\varphi$  is the unit vector along the  $\varphi$  direction.

Taking into account the symmetry of the magnetic vector potential  $\vec{A}$ , it is convenient to solve the corresponding Schrödinger equation in cylindrical coordinates. Utilizing atomic units, in which the Bohr radius is  $0.529 \text{ \AA}$  and the Rydberg energy is  $13.6 \text{ eV}$ , the electron envelope wavefunctions ( $\Psi_{nl}(\rho, z)$ ) and the energy values ( $E_{nl}$ ) are calculated using

$$\left[ -\nabla \left( \frac{1}{m(r)} \nabla \right) + V_{\text{eff}}(\rho, z) \right] \Psi_{nl}(\rho, z) = E_{nl} \Psi_{nl}(\rho, z), \quad (2)$$

where  $\nabla^2$  is the two-dimensional Laplace operator in the  $(\rho, z)$ -plane ( $\rho = r \sin \theta$ ,  $z = r \cos \theta$ ),  $l = 0, 1, 2, \dots$ , is the quantum number of the angular momentum ( $\mathbf{L}$ ) with respect to the  $z$ -axis,  $n$  is the principal quantum number, and  $m(r)$  is the carrier effective mass. The effective potential ( $V_{\text{eff}}(\rho, z)$ ) in equation (2) is given by

$$V_{\text{eff}}(\rho, z) = V(\rho, z) + \frac{1}{m(r)} \left( \frac{l}{\rho} \right)^2 - \frac{\alpha l M}{m(r)} \left( \frac{R}{r_{>}} \right)^3 + \frac{\beta}{m(r)} \left( \frac{R}{r_{>}} \right)^6 (\rho M)^2, \quad (3)$$

where  $\alpha = \frac{8\sqrt{2}\pi}{3c}$ ,  $\beta = \frac{32\pi^2}{9c^2}$ ,  $c = 274.07198$ ,  $M = M_0$  in units of  $\text{Oe}/(4.42537 \times 10^4)$ . In the expression for  $V_{\text{eff}}(\rho, z)$ , the first term is the quantum confining potential induced by the difference in band gap between the nanoparticle and its surrounding, the second term describes the potential associated with the angular momentum and the last two terms represent potentials induced by the magnetization of the magnetized nanoparticle.

In the framework of the FEM, equation (2) can be solved as follows. First, the entire region of the system is divided into elements in real space. For simplicity, we use triangular element meshes. Then any field quantities, e.g. wavefunctions, the wavefunction gradient and the effective potential, are expressed in terms of discretized values at the nodes, whereas values within the elements are determined by linear interpolation using linear shape functions  $N(\rho, z)$ . Thus, for particular shape functions  $N(\rho, z)$  [18, 19], any field in the  $k$ th element is written as

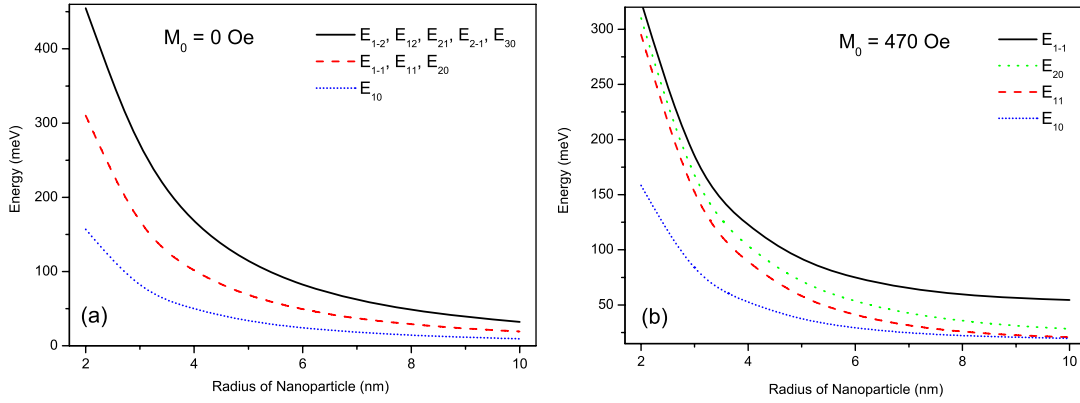
$$\Psi_{nl}^{(k)} = \sum_{j=1}^3 \Psi_j^{(k)} N_j(\rho, z), \quad (4)$$

where the coefficients in the summation are the values of the wavefunction at individual nodes. Finally, using Galerkin’s weighted residue method [18] one obtains the finite element matrix form of the Schrödinger equation in the  $k$ th element as

$$H_{ij}^{(k)} \cdot \Psi_j^{(k)} = \lambda_{nl} \cdot D_{ij}^{(k)} \cdot \Psi_j^{(k)}, \quad (5)$$

where the indices  $i$  and  $j$  range over 1–3. The repeated indices indicate a summation whereas the local element stiffness matrices  $H_{ij}^{(k)}$  and mass matrices  $D_{ij}^{(k)}$  are given by

$$H_{ij}^{(k)} = \iint_{(k)} \left[ \frac{1}{m(r)} \nabla N_i \cdot \nabla N_j + V_{\text{eff}}(\rho, z) \cdot N_i \cdot N_j \right] \rho \, d\rho \, dz \quad (6)$$



**Figure 2.** Electron energy as a function of radius of spherical magnetic nanoparticles, for (a)  $M_0 = 0$  Oe and (b)  $M_0 = 470$  Oe.

and

$$D_{ij}^{(k)} = \int \int_{(k)} N_i \cdot N_j \cdot \rho \, d\rho \, dz. \quad (7)$$

Once the local matrix equations have been calculated for each element, the elements must be jointed in such a way that the wavefunction and its derivatives are continuous at the boundaries. The continuity of the wavefunction is achieved by mapping the local matrix equations for each element onto a single global matrix equation, given by

$$H_{ij} \cdot \Psi_j = \lambda_{nl} \cdot D_{ij} \cdot \Psi_j. \quad (8)$$

This generalized eigenvalue problem is solved for the eigenvalues ( $\lambda_{nl}$ ) and corresponding eigenfunctions ( $\Psi_j$ ) using standard numerical procedures available in numerical analysis packages [18].

### 3. Results and discussion

The experimental observations indicate that both geometrical (size and shape) and physical (effective carrier mass, dielectric constant, band offset, and magnetization) parameters of a magnetic semiconductor nanoparticle play an important role in determining the energy spectrum, number of confined states, and average intershell spacing. All these quantities have a strong impact upon the colloidal stability of ionic colloids based on magnetic semiconductor nanoparticles. To understand the effect of the dipolar magnetic field on the stability of ionic MFs (e.g.,  $\text{Fe}_3\text{O}_4$  nanoparticles dispersed in low or high pH aqueous medium), numerical calculations were performed. The following parameters were used in our calculation:  $m(r) = 0.37$ ,  $V_0 = 400$  meV, and pH12. The probability distribution is defined as  $\rho|\Psi_{nl}|^2$ . The energy reference is chosen at the bottom of the conduction band of the dot material. It is important to emphasize that in the FEM computation the number of elements (NE), the cutoff position ( $r_c$ ) at which the electron wavefunction is zero and the degrees of the interpolation functions are crucial for achieving high numerical accuracy and fast convergence. Therefore, careful attention should be paid while choosing these values [18].

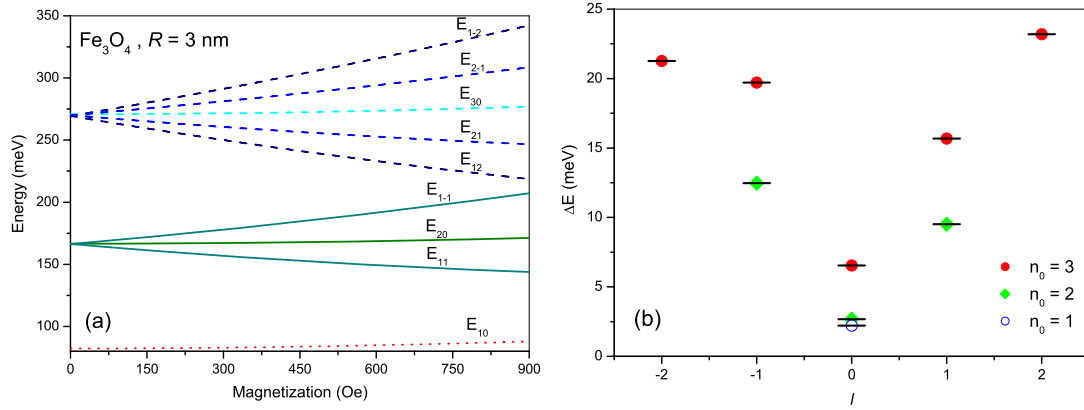
The size dependence of the carrier energy for spherical  $\text{Fe}_3\text{O}_4$  nanoparticles is shown in figures 2(a) and (b) for

$M_0 = 0$  Oe and  $M_0 = 470$  Oe, respectively. It is found that in both cases the carrier energies decrease with increasing nanoparticle size (volume), indicating a reduced quantum confinement effect. In the case of figure 2(a) ( $M_0 = 0$  Oe) there is a degeneracy for each energy level ( $E_{nl}$ ). For instance, for the ground state ( $E_{10}$ ) there is just one atomic orbital and one electron density distribution. However, for the first excited state there are three different atomic orbitals ( $\Psi_{1-1}$ ,  $\Psi_{11}$ , and  $\Psi_{20}$ ) and three different electron density distributions, all states possessing the same energy value ( $E_{20}$ ). Thus, there are three different ways in which the electronic charge may be distributed in three-dimensional space while still possessing the same energy. The dipolar magnetic field of the magnetic nanoparticles, however, removes this degeneracy, splitting the energy level into three distinct energies, as shown in figure 2(b). In addition, the separation among them strongly depends upon the nanoparticle size. For nanoparticles with radius in the range of 2–10 nm, one finds the energy splitting increasing as the nanoparticle size increases.

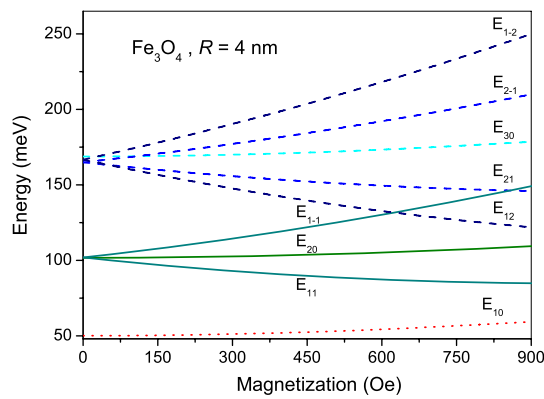
Figure 3(a) illustrates the carrier energy as a function of the magnetization for nanoparticles with  $R = 3$  nm. The energy levels with different  $l$  values present different behaviors. Nevertheless, all energy levels show an almost linear response to the dipolar magnetic field. The sensitivity ( $\Delta E$ ) of the energy level with respect to the dipolar field, which is defined by the difference between the energy at  $M_0 = 900$  Oe and that at  $M_0 = 0$  Oe ( $E_0$ ), is shown in figure 3(b). It is interesting to note that the energy levels for larger  $l$  values are more sensitive to the dipolar magnetic field than those for smaller  $l$  values.

The effect of the magnetization upon the system's behavior can be observed for a nanoparticle with  $R = 4$  nm, as shown in figure 4. The crossover between different energy levels occurs at lower magnetization values for  $R = 4$  nm than for  $R = 3$  nm. In addition, obvious nonlinear magnetic response behavior is also observed. This nonlinearity is attributed to the competition between the quantum confinement effects produced by the barrier height and the magnetic field strength. As the nanoparticle size increases the magnetic field effect becomes the dominating factor.

Figures 5(a)–(c) illustrate the effect of the dipolar field upon the nanoparticle ( $R = 10$  nm) charge density probability



**Figure 3.** Dipolar field dependence of (a) carrier energy and (b) sensitivity ( $\Delta E$ ) of the energy levels for  $R = 3$  nm. The sensitivity is defined as the difference between the energy for  $M_0 = 900$  Oe and the energy for  $M_0 = 0$  Oe ( $E_0$ ).



**Figure 4.** Carrier energy as a function of magnetization for  $R = 4$  nm particles.

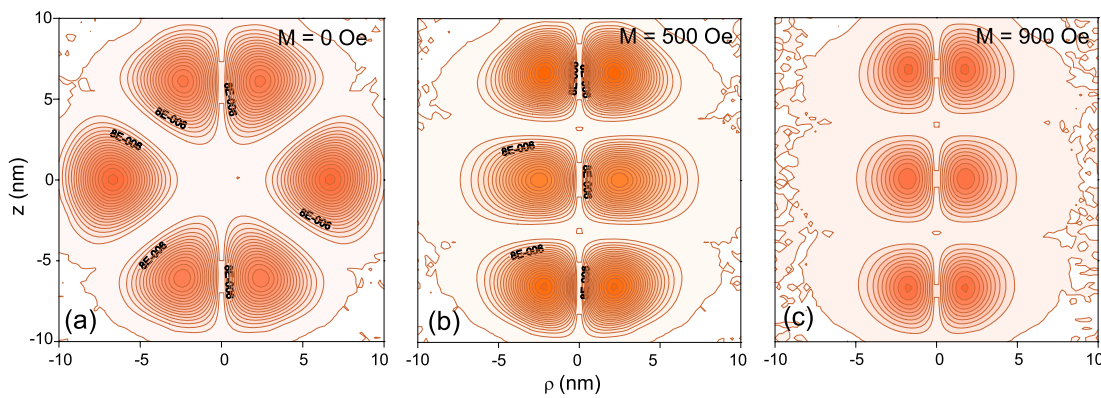
for  $M_0 = 0$  Oe,  $M_0 = 500$  Oe and  $M_0 = 900$  Oe, respectively. Note that the electron density is expressed in terms of the number of electronic charges per unit space volume. Then, the atomic unit of electron density distribution is  $e/a_0^3$ . It is found that the charge density probability distribution is dramatically squeezed by the dipolar magnetic field in the plane perpendicular to the magnetization direction. As a result,

it introduces a strong polarization of the chemical bounds between the nanoparticle surface and the surrounding aqueous-related molecular species (for instance  $\text{OH}^-$ ,  $\text{OH}_2$ , and  $\text{OH}_3^+$ ). Therefore, a considerable effect on the colloidal stability of ionic magnetic fluids is expected. In addition, as a result of the nonuniform anchoring of the molecular species at the nanoparticle surface, one expects a strong influence upon the magneto-optical properties of magnetic fluids.

Figures 6(a) and (b) show the maximum charge density and the corresponding position as a function of the nanoparticle magnetization, respectively. It is found that the maximum charge density increases with increasing magnetization. However, the corresponding position  $r = \sqrt{\rho^2 + z^2}$  shows an opposite behavior.

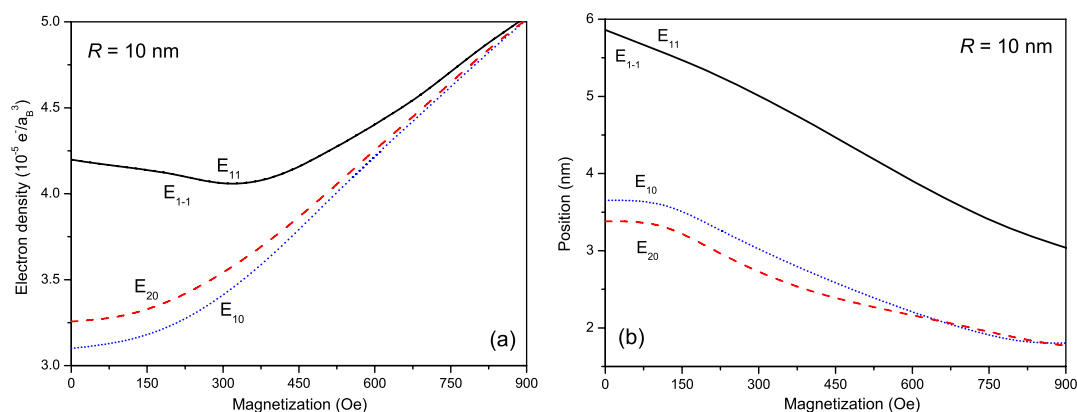
#### 4. Conclusions

The finite element method was successfully applied to solve the challenging nanoscaled problem of finding the effects of the dipolar field on the charge density distribution in a charged magnetic semiconductor nanoparticle. Once the elements shape can be chosen arbitrarily and as long as the boundary conditions are satisfied, the method provides high accuracy results. In addition, since the basis



**Figure 5.** Contour maps of charge density distributions of 4f atomic orbital for  $R = 10$  nm nanoparticles at (a)  $M_0 = 0$  Oe, (b)  $M_0 = 500$  Oe, and (c)  $M_0 = 900$  Oe.





**Figure 6.** Maximum charge density (a) and its corresponding position (b) as a function of the nanoparticle magnetization.

functions are given by strictly local polynomials in real space, the method allows a controlled convergence of the solutions. Permanently magnetized spherical nanoparticles (magnetization  $\mathbf{M}$ ) generate a uniform magnetic field in the inner region and a dipolar magnetic field in the outer region. Effects of the magnetic field on both the carrier energy spectrum and charge density distribution were investigated from the quantum mechanical viewpoint. It was found that the dipolar magnetic field removes the degeneracy of the energy levels, promoting the carrier redistribution among them. Furthermore, the dipolar field changes the charge density distribution, leading to a redistribution of the surface charge density. As a result, it should influence the colloidal stability of ionic magnetic fluids remarkably strongly. These effects depend not only on the magnetization value but also on the nanoparticle size. The larger the nanoparticle size, the bigger the dipolar magnetic field effects. Our observations can be discussed in terms of the competition between the quantum confinement effects introduced by both the particle size and the strength of the dipolar magnetic field.

### Acknowledgments

This work was supported by the Brazilian agencies CNPq, FAPEMIG, CAPES, and FINATEC.

### References

- [1] Rosensweig R E 1985 *Ferrohydrodynamics* (New York: Cambridge University Press) p 1237
- [2] Berkovsky B M, Medvedev V F and Krakov M S 1993 *Magnetic Fluids-Engineering Applications* (Oxford: Oxford University Press)
- [3] Hafeli U, Schutt W and Zborowski M 1997 *Scientific and Clinical Applications of Magnetic Carriers* (New York: Plenum)
- [4] Berkovski B and Bashtovoy V 1996 *Magnetic Fluids and Applications Handbook* (New York: UNESCO)
- [5] Churaev N V 1999 *Adv. Colloid Interface Sci.* **83** 19–32
- [6] Righetto L, Azimonti G, Missana T and Bidoglio G 1995 *Colloids Surf. A* **95** 141–57
- [7] Charnas R, Piazecki W and Rudzinski W 1995 *Langmuir* **11** 3199–210
- [8] Qu F and Morais P C 1999 *J. Chem. Phys.* **111** 8588–94
- [9] Qu F and Morais P C 2000 *J. Phys. Chem. B* **104** 5232–6
- [10] Qu F and Morais P C 2001 *IEEE Trans. Magn.* **37** 2654–6
- [11] Qu F, Oliveira R H and Morais P C 2004 *J. Magn. Magn. Mater.* **272–276** 1668–9
- [12] Qu F, Santos D R Jr, Dantas N O, Monte A F G and Morais P C 2004 *Physica E* **23** 410–5
- [13] Santos D R Jr, Qu F, Alcalde A M and Morais P C 2005 *Physica E* **26** 331–6
- [14] Morais P C and Qu F 2002 *J. Magn. Magn. Mater.* **252** 117–9
- [15] Tronc E, Jolivet J P, Lefebvre J and Massart R 1984 *J. Chem. Soc. Faraday Trans. I* **80** 2619–29
- [16] Bacri J C, Perzynski R, Salin D, Cabuil V and Massart R 1989 *J. Colloid Interface Sci.* **132** 43–53
- [17] Tourinho F A, Campos A F C, Aquino R, Lara M C F L and Depeyrot J 2002 *J. Magn. Magn. Mater.* **252** 29–31
- [18] Qu F Y, Alcalde A M, Almeida C G and Dantas N O 2003 *J. Appl. Phys.* **94** 2130–9
- [19] Johnson H T, Freund L B, Akyuz C D and Zaslavsky A 1998 *J. Appl. Phys.* **84** 3714–25