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Estimation of blocking temperatures from ZFC/FC curves

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Abstract

We present a new method to extract the parameters of a log-normal distribution of energy barriers in an assembly of ultrafine magnetic particles from simple features of the zero-field cooled and field cooled magnetisation curves. The method is established using numerical simulations and is tested on two experimental data sets. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ultrafine particles; Superparamagnetism; Magnetization models

The superparamagnetic relaxation time, τ, of a magnetic nanoparticle is given by $\tau = \tau_0 \exp(E_b/kT)$, where E_b is the energy barrier separating the energy minima, T is the temperature, $\tau_0 \sim 10^{-12}$–10^{-9} s and k is the Boltzmanns constant [1]. In a real sample the dynamic behaviour is extremely sensitive to the inevitable size distribution and it is therefore necessary to take this into account in investigations of the dynamic properties. In this paper we discuss the effect of the particle size distribution on the zero-field cooled (ZFC) and field cooled (FC) magnetisation curves.

The ZFC magnetisation curve is typically obtained by cooling in zero field from a high temperature where all particles show superparamagnetic behaviour to a low temperature and measuring the magnetisation at stepwise increasing temperatures in a small applied field. At each temperature measurements are taken after time t_m. The FC magnetisation curve is typically obtained by measuring at stepwise-decreasing temperatures in the same small applied field after waiting t_m at each temperature. In the following we assume a random orientation of easy axes, a linear relationship between the saturation magnetisation, M, and E_b, a linear relation between the magnetisation and the applied field, and an infinitely sharp transition between superparamagnetic and blocked behaviour. Following Wohlfarth [2] we write the initial susceptibility for a single particle size as $\chi_{sp} = M^2V/3kT$ for $T > T_B(E_B)$ and $\chi_{bl} = M^2/3K$ for $T < T_B(E_B)$, where V is the particle volume, $T_B(E_b) \equiv E_b/[k \ln(t_m/\tau_0)]$ and $K \equiv E_b/V$. The susceptibility of a system of particles with a volume weighted distribution $f(y)$ of reduced energy barriers, $y \equiv E_b/E_{bm}$, where E_{bm} is the median energy barrier, is then

$$\chi_{ZFC}(T) \propto \frac{M^2}{3K}\left[\frac{E_{bm}}{k}\int_0^{T/T_{Bm}} T^{-1} y f(y)\,dy + \int_{T/T_{Bm}}^{\infty} f(y)\,dy\right], \tag{1}$$

where $T_{Bm} \equiv E_{bm}/[k \ln(t_m/\tau_0)]$. The first contribution is from the superparamagnetic particles and the second contribution is from the blocked particles. To model the FC susceptibility we assume that the susceptibility below the blocking temperature is equal to the equilibrium susceptibility at the blocking temperature. We can then write the FC susceptibility as

$$\chi_{FC}(T) \propto \frac{M^2}{3K}\frac{E_{bm}}{k}\left[\int_0^{T/T_{Bm}} T^{-1} y f(y)\,dy + \int_{T/T_{Bm}}^{\infty} [T_B(yE_{bm})]^{-1} y f(y)\,dy\right]. \tag{2}$$

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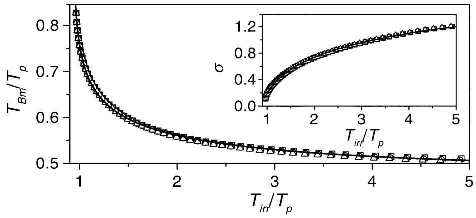

Fig. 1. $T_{\mathrm{Bm}}/T_{\mathrm{p}}$ and σ of the log-normal distribution (inset) as functions of $T_{\mathrm{irr}}/T_{\mathrm{p}}$ for $\tau_0 = 10^{-10}$ s (□), 10^{-11} s (○) and 10^{-12} s (Δ). The full lines are the fits described in the text.

Again the first contribution is from the superparamagnetic particles and the second contribution is from the blocked particles. In the following we consider the log-normal distribution, defined as $f(y)\,\mathrm{d}y = (2\pi)^{-1/2}(\sigma y)^{-1} \times \exp[-\ln^2 y/2\sigma^2]\,\mathrm{d}y$, which has been widely used to describe size distributions of particles [3,4].

Distinct features of a ZFC/FC measurement are a peak of the ZFC magnetisation curve at a temperature T_{p} and that the ZFC and FC magnetisation curves coincide at high temperatures but split at a temperature T_{irr} at which the relaxation time of the largest particles becomes comparable to t_{m}. In the following we define T_{irr} as the temperature at which $\chi_{\mathrm{FC}} - \chi_{\mathrm{ZFC}}$ equals 10% of the susceptibility, χ_{p}, at the peak. When increasing the width of the barrier distribution for a fixed value of T_{Bm}, both T_{p} and T_{irr} will increase reflecting the increasing tail of large particles. This change can be used to obtain information about the parameters of the size distribution. We have found T_{Bm}, T_{p} and T_{irr} as functions of σ in numerical simulations using Eqs. (1) and (2) for $t_{\mathrm{m}} = 100$ s and for different values of τ_0. In Fig. 1 are shown $T_{\mathrm{Bm}}/T_{\mathrm{p}}$ and σ as functions of $T_{\mathrm{irr}}/T_{\mathrm{p}}$. It is seen that the sensitivity to the value of τ_0 (and hence to t_{m}) is weak. Hence, we can obtain unique information about T_{B} irrespective of the value of τ_0. The data were fitted well in the shown range by the phenomenological expressions $T_{\mathrm{Bm}} = T_{\mathrm{p}}[1.792 + 0.186\ln(T_{\mathrm{irr}}/T_{\mathrm{p}} - 0.918)]^{-1} + 0.0039 \times T_{\mathrm{irr}}$ and $\sigma = 0.624 + 0.397\ln(T_{\mathrm{irr}}/T_{\mathrm{p}} - 0.665)$ shown as the full lines in Fig. 1. We have tested this method on two sets of experimental data by comparing the predictions using T_{p} and T_{irr} with the parameters from the fits to Eqs. (1) and (2) and the results obtained by other methods. In Fig. 2 are shown measured ZFC/FC magnetisation data on dilute ferrofluids containing γ-Fe_2O_3 particles and amorphous $Fe_{0.78}C_{0.22}$ particles, respectively. Previous reports and more sample details can be found in Refs. [5] and [4], respectively. The full lines in Fig. 2 are least-square fits to Eqs. (1) and (2). In the insets are shown $\Delta \equiv (\chi_{\mathrm{FC}} - \chi_{\mathrm{ZFC}})/\chi_{\mathrm{p}}$ for the measured data and the fits. The fit is rather poor for the γ-Fe_2O_3 ferrofluid indicating that the log-normal distribution is not completely adequate for describing the barrier distribution as pointed out in Ref. [5]. This can be seen in the inset of Fig. 2A, where the tail of large particles in the fit is overestimated compared to the experimental data. The fit was performed with $\tau_0 = 4 \times 10^{-10}$ s [5] and resulted in $\sigma = 0.75 \pm 0.05$ and $T_{\mathrm{Bm}} = 8.3 \pm 0.5$ K. From the measured data we determine $T_{\mathrm{p}} = 15 \pm 2$ K and $T_{\mathrm{irr}} = 26.7 \pm 1.0$ K. Insertion in the phenomenological expressions given above yield $\sigma = 0.67 \pm 0.11$ and $T_{\mathrm{Bm}} = 8.6 \pm 1.5$ K. The fit to the experimental data for the $Fe_{0.78}C_{0.22}$ ferrofluid (using $\tau_0 = 2 \times 10^{-11}$ s [4]) is much better and resulted in $\sigma = 0.21 \pm 0.02$ and $T_{\mathrm{Bm}} = 18.6 \pm 0.5$ K. We estimate $T_{\mathrm{p}} = 25.0 \pm 0.5$ K and $T_{\mathrm{irr}} = 24.8 \pm 0.5$ K. Using the phenomenological expressions given above we obtain $\sigma = 0.18 \pm 0.05$ and $T_{\mathrm{Bm}} = 19.2 \pm 2.1$ K. These parameters are in good agreement with $\sigma = 0.22$ determined from electron micrographs and $\sigma = 0.20$ and $T_{\mathrm{Bm}} = 18.7$ K determined from a combined analysis of the ZFC magnetisation curve and Mössbauer spectra [4].

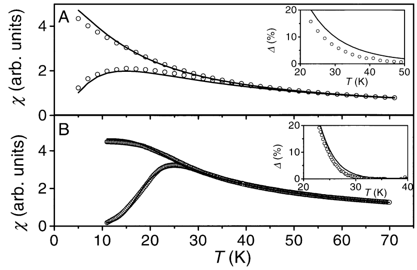

Fig. 2. ZFC/FC magnetisation curves of (A) γ-Fe_2O_3 nanoparticles measured in 3 Oe and (B) amorphous $Fe_{0.78}C_{0.22}$ particles measured in 5 Oe. The full lines are the fits described in the text. In the insets are shown $\Delta \equiv (\chi_{\mathrm{FC}} - \chi_{\mathrm{ZFC}})/\chi_{\mathrm{p}}$ for the data (points) and the fits (lines).

We have used a simple model for ZFC/FC measurements to fit two sets of experimental data. The same models were used in numerical simulations to find $T_{\mathrm{Bm}}/T_{\mathrm{irr}}$ and σ as functions of $T_{\mathrm{p}}/T_{\mathrm{irr}}$ and good agreement was found between the parameters obtained from the fits to Eqs. (1) and (2) and those obtained using the approximate method based on T_{p} and T_{irr}. Thus, the method provides a way to get a quick estimate of T_{B} and σ without doing any computer analysis of the data. It is therefore an alternative method to the one by Chantrell et al. [3] in which σ and the median diameter, D_{V}, are estimated using the behaviour at low and high fields, respectively. The method by Chantrell et al is sensitive to an intrinsic high-field susceptibility, while the present method only uses a low applied field. On the other hand the present method neglects the temperature variation of M which may result in erroneous results if the material has a low Curie temperature.

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