Relationship between blocking temperature and strength of interparticle interaction in magnetic nanoparticle systems

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Abstract

In magnetic nanoparticle systems, the variation of the blocking temperature T_B with the measuring frequency f_m is often used to determine the strength of the interparticle interactions (IPI) through a parameter Φ or the Vogel-Fulcher temperature T_o . Presence of IPI is inferred if $T_o > 0$ and $\Phi = \Delta T_B / [T_B \Delta \log_{10} f_m] < 0.13$ where Δ signifies changes in T_B and f_m . Here it is shown that these two parameters are related by the Eq. $\Phi = \Phi_o [1 - (T_o/T_B(1))]$ where $\Phi_o \approx 0.11$ to 0.15 is a constant of the system depending on the magnitudes of measuring frequency and the attempt frequency f_o of the Néel relaxation. Using data on a variety of nanoparticle systems, experimental verification of this relationship is also presented.

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1. Introduction

Magnetic properties of materials in reduced dimensions (thin films, wires and nanoparticles) continue to attract world-wide attention for two reasons: the emergence of new scientific phenomenon and potential applications of materials with reduced dimensions [1-4]. For magnetic nanoparticles (NPs), potential applications include tumor therapy by magnetic hyperthermia, targeted drug delivery, MRI contrast agents and biosensors [5-10]. An important property of magnetic NPs is their blocking temperature T_B which separates the superparamagnetic (SPM) state for temperatures $T > T_B$ from the frozen magnetic state for $T < T_B$. For many biomedical applications, the NPs need to be in the SPM state at room temperature requiring $T_B < 300$ K so that the NPs are only magnetic in an applied magnetic field H without any residual magnetization (M) when H is removed. Thus determination of the blocking temperature of a nanoparticle system is usually the first property to be measured.

For defining the blocking temperature T_B , consider a system of nanoparticles (NPs) each with volume V and uniaxial anisotropy constant K_a . At a temperature T and in the absence of any interparticle interactions (IPI), the rate of flipping f of the magnetic moment of the particle against the energy barrier $E_a = K_a V$ is given by the Néel-Brown relaxation [11, 12]:

$$f = f_o \exp(-E_a/k_B T) \text{ ----- (1).}$$

In Eq. (1), k_B is the Boltzmann constant and f_o is the system-dependent attempt frequency varying only weakly with temperature as discussed at some length later. An anisotropy related temperature $T_a = E_a/k_B$ may be conveniently defined. From Eq. (1), when f becomes equal to f_m , the frequency of measurement, then the system will appear to be blocked below the blocking temperature T_B given by

$$T_B = T_a / \ln(f_o / f_m) \text{ ----- (2).}$$

Eq. (2) is not valid in the presence of IPI whose strength depends on particle concentration, their size and size distributions, and on the nature of the matrix. Contributions to the IPI can come from several sources. For NPs with magnetic moment μ separated by distance r , $E \sim \mu^2 / 4\pi r^3$ is the interaction energy from the dipole-dipole interaction. If the particles are uncoated and in close contact, even the exchange interaction may become significant. When the matrix and the particles are both metallic, then the RKKY (Ruderman- Kittel-Kasua-Yosida) interaction varying as $1/r^3$ may become important. In addition, the presence of strong IPI may lead to a low-temperature collective state with long-range order such as super-ferromagnetism or super-spin glass state [13]. Thus, determining the strength of IPI and its effects on the measured properties in a nanoparticle system is an important issue for understanding its magnetic properties.

Computationally [14-16] and experimentally [17-19], it is now known that the presence of IPI raises the magnitude of the blocking temperature T_B by an effective temperature T_o representing the strength of the IPI among the NPs. For the case of $T_o < T_B$ Eq. (1) is often replaced by the Vogel-Fulcher law [20-21] given by

$$f = f_o \exp[-E_a / k_B(T - T_o)] \text{ ----- (3).}$$

Eq. (3) was also proposed by Tholence [21] for spin glasses with the frequency dependence of the freezing temperature T_f replacing T_B . Additional discussion and analysis on the use and limits of Eq. (3) for super-paramagnets and spin glasses is given in the paper by Dormann et al [22]. The use of Eq. (3) leads to a new relationship for T_B , replacing Eq. (2), in which T_B is enhanced by T_o :

$$T_B = T_o + T_a / \ln(f_o / f_m) \text{ ----- (4).}$$

Experimentally, the presence of IPI in a magnetic nanoparticle system can be detected by comparing the magnitudes of T_B at a fixed f_m with and without magnetic dilution since T_B will be lower with magnetic dilution, such as coating of the particles with a surfactant [18, 19]. An alternative approach to detecting the presence of IPI is determining how T_B in a system varies with the change in the measuring frequency f_m . For this purpose, a quantity Φ has been defined as [22]:

$$\Phi = \Delta T_B / [T_B \Delta \log_{10} f_m] \text{----- (5).}$$

In Eq. 5, ΔT_B is the change in T_B with change in f_m written in terms of $\Delta \log_{10} f_m$. T_B is usually defined as the position of the peak in the out-of-phase ac magnetic susceptibility χ'' measured at a particular f_m . The magnitude of Φ is known to vary with the strength of IPI; $\Phi \geq 0.13$ for non-interacting particles, $0.05 < \Phi < 0.13$ for interacting particles with Φ decreasing with increase in the strength of IPI and $\Phi < 0.05$ for spin-glasses [22]. Since both T_o and Φ have been used in the literature to provide a measure of the strength of the IPI in a system, it is instructive to determine whether a relationship exists between these two parameters. In this paper, we derive such a relationship and verify its validity using our own yet unpublished data on four oleic-acid coated maghemite NPs with average sizes of 2.5 nm, 3.4nm, 6.3 nm and 7.0 nm [23] as well as data from published papers in a number of nanoparticle systems where the magnitude of both T_o and Φ are available.

2. Derivation of the relationship between T_o and Φ

Consider measurements of T_B in a system using two different measuring frequencies $f_m(1)$ and $f_m(2)$ with $f_m(2) > f_m(1)$. Applying Eq. (4) yields

$$T_B(1) = T_o + T_a / [\ln f_o - \ln f_m(1)] \text{----- (6)}$$

and

$$T_B(2) = T_o + T_a/[\ln f_o - \ln f_m(2)] \text{ ----- (7).}$$

Using equations (6) and (7), $\Delta T_B = T_B(2) - T_B(1)$ is calculated and substituted in Eq. (5) to determine Φ . After some simplifications, the following equations are derived without any approximation:

$$\Phi = \Phi_o \{1 - [T_o/T_B(1)]\} \text{ ----- (8),}$$

$$\Phi_o = 2.3026/\{\ln[f_o/f_m(2)]\} \text{ ----- (9).}$$

From Eq. (9), the magnitude of Φ_o is a constant of the system in that it depends on the attempt frequency f_o and measuring frequency $f_m(2)$. Usually, f_o varies between 10^9 Hz to 10^{12} Hz for different systems as discussed later and f_m in commercially available experimental systems can be varied from a low value of 0.1 Hz to high value of 10^4 Hz. As examples, using Eq. (9), if $f_o = 10^{10}$ (10^9) Hz and $f_m(2) = 10^3$ Hz, then $\Phi_o = 0.143$ (0.167) is obtained. Similarly for $f_o = 10^{12}$ Hz and $f_m(2) = 10^4$ Hz, $\Phi_o = 0.125$ is obtained. For the often quoted $\Phi_o = 0.13$, $f_o/f_m(2) = 4.9 \times 10^7$ is needed. Eq. (8) relating Φ to the fractional change $T_o/T_B(1)$, along with Eq. (9) for Φ_o , and the experimental verification of Eq. (8) given below are the new results of this paper.

3. Experimental Results and Discussion

For experimental verification of Eq. (8) connecting Φ , T_o and Φ_o , the literature was searched to find magnetic nanoparticle systems where magnitudes of Φ , $T_B(1)$ and T_o have been published by the authors. The magnitude of Φ is easily determined using Eq. (5) if T_B is measured for at least two sufficiently different frequencies. Following Eq. (4), determination of f_o and T_o and consequently T_a can be done by plotting $\ln f_m$ vs. $1/(T_B - T_o)$ for different choices of T_o until

the data of T_B at different f_m values falls on a straight line for a given choice of T_o [24-27]. The intercept on the ordinate then yields f_o and the slope T_a . Based on these considerations, the plot of Φ versus $T_o/T_B(1)$ is shown in Fig. 1 with each data point belonging to a different system. Included here are our data of Φ , T_o and Φ_o on four oleic-acid coated maghemite NPs with average sizes of 2.5 nm, 3.4nm, 6.3 nm and 7.0 nm [23, 24] along with the data on 3 nm Fe/Pt core-shell NPs [25]. The other systems included here are 3 nm and 9 nm FePt NPs [26], Ni-SiO₂ NPs [27], and NiO NPs [28]. The data on the systems Fe-Al₂O₃, ZnCr_{1.6}Ga_{0.4}O₄ [29], CdCr_{1.7}In_{0.3}S₄ [30] and CsNiFeF₆ [31] are tabulated in the paper by Dormann et al [22]. The plot of Φ versus $T_o/T_B(1)$ should yield a straight line if Eq. (8) is valid with the intercept yielding the magnitude of Φ_o . Overall, the data follows the predicted linear variation of Φ with $T_o/T_B(1)$ with the two dotted lines drawn for $\Phi_o = 0.11$ and $\Phi_o = 0.15$ bracketing most of the data points. In Fig. 1, the numbers in [] adjacent to each system represent reference to the publication from which the data is taken. The scatter in the data points around the predicted linear behavior likely results from different magnitudes of the ratio $f_o/f_m(2)$ and hence Φ_o in different systems since f_o is indeed somewhat system dependent and not a constant as discussed below.

The Brown model for thermal relaxation of superparamagnetic NPs [12, 22] gives the following equation for f_o :

$$f_o = 2\gamma_o(T_a/\pi T)^{1/2}k_B T_a/\mu_p \text{-----} (10).$$

In Eq. (10), $\gamma_o = 2\pi g\mu_B/h = 1.759 \times 10^7$ is the gyromagnetic ratio for $g=2$, μ_p is the magnetic moment of the NP and T_a is the effective anisotropy temperature defined in Eq. (2). According to Eq. (10), f_o depends on the system parameters T_a and μ_p . However, the $T^{-1/2}$ temperature dependence of f_o evident in Eq. (10) is much weaker than the exponential temperature dependence

of f in Eq. (2) and Eq. (3) so that f_o may be considered to be relatively constant in a limited temperature range where Eq. (2) and Eq. (3) are applied.

As examples of the calculations of f_o and Φ_o , we use the published parameters for 7.0 nm NPs of maghemite for which $T_a = 725$ K and $\mu_p = 7500 \mu_B$ have been reported [24]. Substituting these values in Eq. (10) yields $f_o = 44$ GHz at $T = 300$ K, comparing favorably with the experimental $f_o = 26$ GHz determined from fitting the data of T_B at different f_m to Eq. (4). If $T = T_B = 35$ K is used, then $f_o = 129$ GHz is obtained. Using $f_o = 26$ GHz (129 GHz) and experimental $f_m(2) = 5$ kHz in Eq. (9) yields $\Phi_o = 0.149$ (0.135). This illustrates some system and temperature dependent variations in the magnitude of Φ_o as argued above.

4. Conclusions

In this paper, it is shown that the two parameters Φ and T_o usually used to determine the strength of the interparticle interactions in magnetic nanoparticle systems are related by Eq. (8) with Φ_o given by Eq. (9). The experimental verification of this relation is presented in Fig. 1 using data on a variety of nanoparticle systems. The magnitude of $\Phi_o \approx 0.13$ often quoted in papers really depends on the ratio $f_o/f_m(2)$ for each system and so it may differ somewhat from this magnitude as shown in representative calculations given above. The above derivation depends on the validity of the Vogel-Fulcher relation (Eq. 3) for a system.

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Figure Captions:

Figure 1: Verification of Eq. (8) by plotting Φ versus (T_o/T_B) for different systems listed in the legend of the figure. The solid circles are experimental data points with experimental uncertainties shown for cases where this information was available. The two dotted lines represent Eq. (8) with $\Phi_o = 0.15$ and 0.11 . The numbers in [] give reference to the paper from which data are taken.

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Figure 1: Verification of Eq. (8) by plotting Φ versus $(T_o/T_B(1))$ for different systems listed in the legend of the figure. The solid circles are experimental data points with experimental uncertainties shown for cases where this information was available. The two dotted lines represent Eq. (8) with $\Phi_o = 0.15$ and 0.11. The numbers in [] give reference to the paper from which data are taken.