Mössbauer spectra of ferrofluids characterized using a many state relaxation model for superparamagnets

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Using a many-state relaxation formalism and combining it with an accurate expression for the relaxation time of single-domain ferromagnetic particles and a log-normal size distribution we are able to fit Mössbauer spectra which span temperatures from where a pure hyperfine field distribution is present to where a single broad line occurs due to high relaxation rates. With this model, we have fitted the Mössbauer spectra of two Fe_3O_4 ferrofluids, from 12 to 180 K. Fits to the ferrofluid with a mean particle size of 4.5 nm yield an anisotropy energy (K) of $3.0\pm0.1\times10^4$ J/m^3 with the onset of magnetic relaxation at 30 ± 5 K while data for a mean particle size of 6.0 nm give $K=2.4\pm0.2\times10^4$ J/m^3 with magnetic relaxation starting at 55 ± 5 K. These blocking temperatures agree with those extrapolated from frequency dependent χ_{ac} data. © *2000 American Institute of Physics.* [S0021-8979(00)66608-2]

I. INTRODUCTION

Thermal agitation can cause the magnetization direction of a single-domain particle to fluctuate. The internal magnetic potential energy of such a particle can be characterized by the expression $E=-KV\cos^2(\theta)$ where K is the anisotropy constant of the particle, V its volume, and θ the angle between the easy axis of the particle and the direction of magnetization. At low temperatures, the magnetic moment of the particle will remain fixed along an easy axis (blocked). As temperature increases, the magnetic moment will oscillate around the easy axis (collective excitations) with larger amplitude as it gets warmer, until it starts to jump over the energy barrier between the two easy directions with a relaxation time τ.

At low temperatures, collective excitations of single-domain particles have been modeled by Mørup.[1] It is assumed that the fluctuations around the easy axis occur much faster than the Larmour precession of the Mössbauer atoms. The probability of the magnetic moment being at an angle away from an easy axis is calculated, resulting in a correction to the hyperfine field. The asymmetric lineshape of the sextet that is the signature of single-domain particles at low temperatures is correctly predicted. At high temperatures, where reversals of the magnetic moment occur, Mössbauer spectra of single-domain particles are generally modeled using stochastic two level lineshape formalisms, such as the one by Blume and Tjon.[2] At some intermediate temperature, when there is just enough thermal energy for the magnetization direction of particles to start reversing, Mössbauer spectra appear composed of approximately equal areas of magnetically split and unsplit components. This temperature is called the blocking temperature (T_B).[3] The models for collective excitations and spin flipping cannot predict spectra in this intermediate temperature regime, except by assuming that spectra are composed of some linear combination of the two above models.[4] Without a model which can predict spectra over the entire range of temperatures, determining T_B can be problematic.

In real systems, the situation is generally complicated by a distribution of particle sizes and interparticle interactions.[4] Interparticle interactions result in a reduction of K,[5] as they effectively reduce the oscillation amplitude necessary for reversal of the magnetization direction. A distribution of particle sizes ensures that for a real system, at a given temperature, some particles will undergo collective excitations while others will be superparamagnetic. Only in the simplest case of very dilute fine particle systems with a narrow distribution of particle sizes, where interparticle interactions are considered to be absent,[4] can Mössbauer spectra be modeled with any certainty. This is because spectra of such systems clearly consist of a magnetic sextet and doublet. The definition of T_B, which depends upon equal areas of sextet and doublet, is useful for such spectra. In fine particle systems with a broad distribution of particle sizes, it is very difficult to apply this definition as the full range of behavior is present at the intermediate temperature regime that T_B occurs. A combination of the two above models has been used to fit such spectra, however, linewidths were allowed to increase with temperature,[6–8] an incorrect approach as it masks a characteristic mark of magnetic relaxation.

We present a solution to the problem when interparticle interactions and a broad particle size distribution are present. We have used the many level formalism of Jones and Srivastava[9] as a starting point and combined this with an approximation to the analytic solution of the relaxation time, valid for small energy barriers,[10] and a log-normal particle size distribution. We are able to predict the lineshape of spectra at all temperatures describing the full range of behavior of single-domain particles. This model has allowed us to calculate relaxation rates and the anisotropy energy as well as unambiguously determine T_B. Fits to spectra of two ferrofluids yield results in agreement with those from other techniques.

II. EXPERIMENTAL METHODS

We have studied two commercial Fe_3O_4 ferrofluids.[11] Particle size distributions determined by electron micro-

graphs were supplied which gave $\ln(\sigma_D)=0.2$ for the 4.5 nm ferrofluid and $\ln(\sigma_D)=0.225$ for the 6.0 nm ferrofluid. χ_{ac} data was collected using a Quantum Design Physical Properties Measurement System (PPMS) at temperatures from 5 to 300 K with the sampling frequencies of 10 to 10 kHz. Assuming an exponential time dependence with respect to a measurement time of 10^{-8} s, blocking temperatures for the Mössbauer measurements were extrapolated to lie around 26 ± 4 K for the 4.5 nm ferrofluid and 55 ± 2 K for the 6.0 nm ferrofluid.

Transmission Mössbauer measurements were done with a constant acceleration spectrometer using a 1 GBq ^{57}Co**Rh** source calibrated using α-Fe at room temperature. Spectra were collected at temperatures ranging from 12 to 180 K, where the carrier liquid of the ferrofluid started to melt and Brownian motion started to wash out the spectra.

Starting with the assumption that the ferromagnetic particles experience uniaxial anisotropy,[8] we defined the magnetic energy of a particle with $E=-KV\cos^2(\theta)$. The lineshape expression $I(\omega)=2\,\mathrm{Re}(\mathbf{WM^{-1}1})$ is solved with ω the energy of the γ ray and **1** a unit vector. **W** is a row vector with its N components being proportional to the occupation probabilities of the states in equilibrium, evaluated as $W_i=\exp(-E_i/k_BT)$. The matrix **M** contains the description of the system, including the hyperfine field and the relaxation rate, in terms of line positions and its generating functions are given in the article by Jones and Srivastava.[9] It essentially maps the difference between the two potential wells of the magnetic particle as a series of levels. This model allows us to describe the results of various tilt angles that the magnetization vector of the particle can make. Thus collective excitations, interparticle interactions, and superparamagnetism are described with one formalism.[12] To calculate the relaxation rate for a particle, the expression from Coffey *et al.*[10] which is valid to within 0.5% of the exact analytic solution[4] was used. Rates for all particle sizes of the log-normal distribution could be determined, and were used to sum the resulting subspectra. By specifying temperature as well as the mean and standard deviation of the log-normal particle size distribution, using a least-squared fitting method, only seven adjustable parameters were necessary to describe all the spectra.

III. RESULTS AND DISCUSSION

Some of the spectra collected with the 4.5 nm ferrofluid can be seen in Fig. 1. Similar results were obtained with the 6.0 nm ferrofluid. We clearly see line asymmetry at low temperatures. As well, there is a sextet component to the spectra over a large range of temperatures, unlike the swift collapse within the small temperature range seen in paramagnetic to ferromagnetic transitions.[4]

With our model, 25 levels were used to fit the spectra. With fewer levels spectra could not be fitted and more levels simply increased computation time. For low temperature spectra, the hyperfine field was a fitted parameter at 50.04 ±0.06 T, however, as relaxation effects became dominant, the field was fixed at 50 T, removing any possible correlations between hyperfine field and relaxation rate. The effectiveness of our model is corroborated with a less than 4% variation in fitted linewidths for all the spectra.

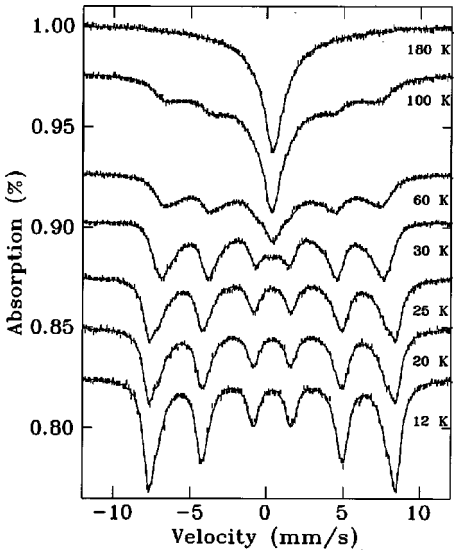

FIG. 1. Mössbauer spectra of the 4.5 nm ferrofluid. Similar spectra were recorded with the 6.0 nm ferrofluid.

Fits to the Mössbauer spectra, shown in Fig. 2, yielded $T_B=30\pm5$ K for the 4.5 nm ferrofluid and $T_B=55\pm5$ K for the 6.0 nm ferrofluid. Comparison of these values with our χ_{ac} data clearly shows that our model allows T_B to be determined correctly and compared with other probes sensitive to magnetic relaxation. For the 4.5 nm ferrofluid, $K=3.0\pm0.1\times10^4$ J/m^3 and for the 6.0 nm ferrofluid $K=2.4\pm0.2\times10^4$ J/m^3, in agreement with previous measurements of similar magnetite fine particle systems.[13–15] A lower K for the 6.0 nm ferrofluid is indicative of stronger interparticle

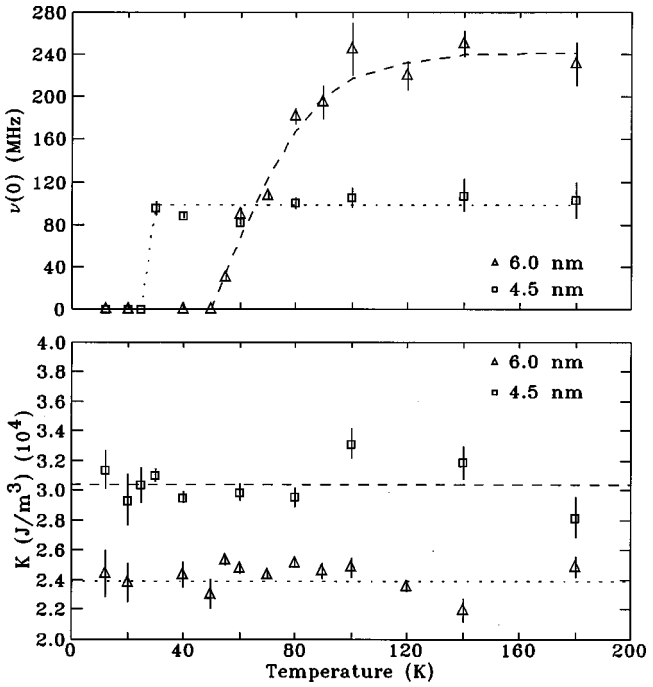

FIG. 2. Plots of the preexponential factor of the relaxation time $\nu(0)$ and the anisotropy energy K. T_B is the point where $\nu(0)>0$.

interactions. With the broader distribution of particle sizes in the 6.0 nm ferrofluid, stronger interparticle interactions are expected. The 4.5 nm ferrofluid relaxation times are much smaller than the 6.0 nm ferrofluid times and the increase in rates much more abrupt. This is consistent with the smaller particles and smaller range in particle sizes.[15]

IV. CONCLUSIONS

We have developed a model which describes the behavior of Mössbauer spectra of fine particle systems over the complete range of temperatures. Results of this description have been verified with other experimental probes. Comparison of blocking temperatures using our Mössbauer effect model and ac susceptibility data are in agreement. Values of K are similar to previous studies of fine particle systems, falling into the expected range of 10^4-10^5 J/m^3.[13–15] For temperatures higher than T_B, relaxation rates used to describe the spectra fall in the typical time region of $\tau = 10^{-8}-10^{-9}$ s.

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