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Experimental study on T_2 relaxation time of protons in water suspensions of iron-oxide nanoparticles: Effects of polymer coating thickness and over-low $1/T_2$

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ABSTRACT

The T_2 relaxation time of protons in three sets of water suspensions of polymer coated Fe_3O_4 particle clusters with effective diameter of the order of 10^2 nm is measured. It is found that with increasing the effective average coating thickness, the waiting time t_w dependence of the measured T_2 is weakened, but the T_2 at $t_w = 0$, $T_2(0)$, remains almost without change, having the values of relaxation rate $1/T_2(0)$ substantially lower than its static dephasing limit. The weakened t_w dependence is a consequence of the weakened magnetostatic interaction, which induces cluster aggregation; the stable $T_2(0)$ can be justified in the framework of existing theories; and the over-low $1/T_2(0)$ is an interesting phenomenon, whose origin deserves further research.

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1. Introduction

The synthesis and characterization of superparamagnetic iron-oxide (Fe_3O_4 or Fe_2O_3) particles recently became an intensively studied topic owing to their potential technological and medical applications [1–3]. They can be used as contrast agents in magnetic resonance imaging (MRI) to increase the relaxation rate of water protons. Theoretical studies show that the increased transverse relaxation rate $1/T_2$ of protons in a high dc field H_0 is a function of the magnetization, sizes, and volume fraction of the particles [3–8]. For a given iron-oxide material of fixed volume fraction, $1/T_2$ increases and then decreases with increasing the particle size, showing a broad maximum around a size of $\sim 10^2$ nm.

The existing theories are qualitatively in agreement with experimental data and they are widely used as a guidance in experimental work [7,9–12]. However, as stated in [4], analytically derived theoretical results have to be fully validated by compar-

ison with computer simulations or actual experiments. Previous validation has been done by Monte Carlo simulations with consistent results. This is expectable since analytical and numerical calculations are based on essentially the same basic assumptions. On the other hand, to the best of our knowledge, a serious quantitative comparison between theoretical and experimental results has not been done, mainly owing to the difficulties in the determination of the size distribution of magnetic particles and to the strong tendency of particle aggregation in large magnetic fields. In fact, the experimental validation can be more important when the assumptions, based on which theoretical calculations are performed, themselves are an approximate expression of the reality.

We consider particles to be spherical with radius R . When $2R < 10$ nm, the theoretically predicted $1/T_2$ is roughly proportional to R^2 , so that an accurate determination of R becomes vital for the comparison with experimental data. Since iron-oxide particles often have a wide size distribution and an organic shell of unknown thickness, their average R measured by different techniques can be significantly different. This difficulty has been overcome in [13], where a technique of particle size determination from magnetization measurements is proposed. Using a certain average particle size determined by this technique, the measured $1/T_2$ of water suspensions of superparamagnetic iron-oxide

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particles of commercial products Resovist and SH U555C has been compared with its theoretical values [14]. It is found that the theoretical $1/T_2$ is larger than the experimental one by about 20% for both cases, and the difference may be reasonably attributed to the effect of organic coating. This conclusion is not only an experimental validation of the existing theories but also different from a popular belief that clustering has a key effect on $1/T_2$ of water suspensions of one of both products [7].

When $2R$ is around 10^2 nm, the theoretically predicated $1/T_2$ is a weak function of R , so that an accurate determination of R becomes less important for a proper comparison between theoretical and experimental results, and the difficulty will come from the field induced particle aggregation. Such large particles cannot be single domain as required by classical superparamagnetism, and they are usually nanoparticle clusters. As studied in [15], a suspension of such clusters behaves superparamagnetically at low magnetic fields, with the magnetic moment of each cluster being equal to the saturation moment of about 20 constituent nanoparticles if the cluster is not too small. The moment of each cluster increases with increasing applied field until its saturation value is reached. Thus, a stable suspension at zero field will become unstable when a high field H_0 is applied during T_2 measurements, owing to cluster aggregation driven by hugely increased magnetostatic interactions among the clusters. This effect causes the measured T_2 to be highly magnetic history dependent.

However, there is an important phenomenon, i.e., the waiting time t_w dependence of the measured T_2 after inserting the sample, which has never been magnetized by a strong field, into the gap of the magnet of the instrument, found in our previous experimental study on T_2 of protons in water suspensions of iron-oxide particle clusters [16]. From the initial portion of the measured $T_2(t_w)$, $T_2(0)$ in the stable state at earth field without cluster aggregation can be obtained by a power-law extrapolation to $t_w = 0$. Thus, the complicated history dependence of T_2 is avoided and the experimental $1/T_2(0)$ can serve as a proper quantity to be compared with the theoretical $1/T_2$.

Applying this technique, we will study in the present work the T_2 of three sets of suspensions of Fe_3O_4 /polymer microspheres with different polymer coating thicknesses. We will show that the t_w dependence for such composite microspheres with thicker coating is weaker, which is expected by a weaker magnetostatic interaction, and that $1/T_2(0)$ is practically independent of coating thickness and is smaller than what is predicted by existing theories, which is an interesting phenomenon to be understood.

The samples and measurements are described in Section 2. Section 3 is devoted to a brief description of the existing theories of T_2 , which is necessary for the treatment, analysis, and explanation of experimental data. The measured results of T_2 are shown in Section 4. The determined $1/T_2(0)$ as a function of particle size is analyzed and compared with existing theories in Section 5. The coating independent over-low $1/T_2(0)$ is discussed in Section 6, based on which the coating-thickness dependent waiting time dependence is discussed in Section 7. The conclusions of practical or theoretical importance are presented in Section 8.

2. Samples and measurements

Fe_3O_4 nanoparticles were prepared by coprecipitation and then modified by oleic acid. The resultant particles form composite microspheres A by self-assembly effect of hydrophobic Fe_3O_4 nanoparticles [17]. Microspheres B and C, were synthesized through hybrid miniemulsion polymerization using A as magnetic cores [18,19], and the obtained magnetic microspheres were

Table 1
Properties of suspensions A, B, and C.

Sample	A	B	C
f_m	0.783	0.288	0.075
ζ (mV)	−36	−46	−48
$1/T_2(0)$ (s ^{−1})	28.3	25.3	26.2
$2R$ (nm)	156	98	98
$2R_{\text{comp}}$ (nm)	214	230	390
τ_D (μ s)	2.0	0.80	0.80
$\tau_{D,\text{comp}}$ (μ s)	3.8	4.4	12.7
$U_{\text{mag}}/k_B T$	−2500	−120	−29
$U_{\text{elec}}/k_B T$	90	160	300

f_m is the mass fraction of polymer in powder, ζ is zeta potential of suspensions, $T_2(0)$ is the $T_2(t_w)$ of suspensions extrapolated to $t_w = 0$ for volume fraction $f_v = 10^{-6}$, $2R$ is the effective average diameter of Fe_3O_4 microspheres (or aggregates of microspheres for A), $2R_{\text{comp}}$ is the average diameter of composite microspheres (or aggregates of microspheres for A), τ_D and $\tau_{D,\text{comp}}$ are the water molecular diffusion times corresponding to the microspheres and composite microspheres, respectively, and U_{mag} and U_{elec} are the magnetostatic and electrostatic interaction energies between two touching composite microspheres (or aggregates for A).

coated by a styrene and acrylic acid copolymer shell. Acrylic acid also provided carboxyl on the microsphere surface.

Each set of microspheres was dispersed in 0.1 wt% sodium dodecyl sulfate (SDS) solution in order to make the suspensions stable. Zeta potential for the suspensions with pH ≈ 7 was measured using a zeta potential sizer (ZPS, Zeta 2000, Malvern, UK) to be $\zeta = -36, -46$, and -48 mV for A, B and C, respectively. They are listed in Table 1.

Representative images of transmission electron microscopy (TEM, JEM100CX, JEOL, Japan) for microspheres A–C are shown in Figs. 1(a)–(c), respectively. The hydrodynamic size distribution by volume, measured by dynamic light scattering (DLS, HPP5001, Malvern, UK), is shown in Fig. 2. The mass fraction f_m of Fe_3O_4 in powder was determined by thermogravimetric analysis (TGA/DSC 1/1600, Mettler Toledo, Switzerland) to be 0.783, 0.288, and 0.075 for powders A, B, and C, respectively. They are listed in Table 1. With such f_m and density 5200 kg m^{-3} for Fe_3O_4 [20], the magnetization of Fe_3O_4 particles $\mu_0 M = 0.45 \text{ T}$ was measured for a sample of powder A by a SQUID magnetometer (MPMSXL7T, Quantum Design, USA) at field $\mu_0 H = 1.41 \text{ T}$ and $T = 310 \text{ K}$. Since the original data given by the magnetometer is the moment m of the sample in emu units, it may be useful to give here the formula to calculate $\mu_0 M$ in SI units: $\mu_0 M = 4\pi m \rho / (10\,000 w f_m)$, where w and ρ are the sample mass and the density of Fe_3O_4 , respectively, in cgs units.

T_2 was measured by a low-resolution NMR spectrometer (Minispec, mq60, Bruker, Germany), whose proton resonance frequency was 60 MHz, corresponding to the applied magnetic field $\mu_0 H_0 = 1.41 \text{ T}$. The Carr–Purcell–Meiboom–Gill (CPMG) spin-echo sequence was adopted with the echo time $\tau_{\text{CP}} = 0.5 \text{ ms}$. For each set of suspensions, the volume fraction f_v of iron oxide in the starting suspension was determined by inductively coupled plasma emission spectroscopy (ICP, ICAP6300, Thermo Fisher, USA). The NMR samples of 0.2 mL volume and different values of f_v were diluted from the starting suspension and filled in the NMR tube. They were heated in a 310 K water bath before T_2 measurements at the same temperature.

3. Theories of T_2

As first described by Bloch [21], the magnetic moments of nuclei in normal matter will result in a nuclear paramagnetic

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