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Molecular dynamics simulations of proton transverse relaxation times in suspensions of magnetic nanoparticles

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ABSTRACT

In this work we have analyzed the influence of various factors on the transverse relaxation times T_2 of water protons in suspension of magnetic nanoparticles. For that purpose we developed a full molecular dynamics force field which includes the effects of dispersion interactions between magnetic nanoparticles and water molecules, electrostatic interactions between charged nanoparticles and magnetic dipole–dipole and dipole–external field interactions. We also accounted for the magnetization reversal within the nanoparticles body frames due to finite magnetic anisotropy barriers. The force field together with the Langevin dynamics imposed on water molecules and the nanoparticles allowed us to monitor the dephasing of water protons in real time. Thus, we were able to determine the T_2 relaxation times including the effects of the adsorption of water on the nanoparticles' surfaces, thermal fluctuations of the orientation of nanoparticles' magnetizations as well as the effects of the core–shell architecture of nanoparticles and their agglomeration into clusters. We found that there exists an optimal cluster size for which T_2 is minimized and that the retardation of water molecules motion, due to adsorption on the nanoparticles surfaces, has some effect in the measured T_2 times. The typical strengths of the external magnetic fields in MRI are enough to keep the magnetizations fixed along the field direction, however, in the case of low magnetic fields, we observed significant enhancement of T_2 due to thermal fluctuations of the orientations of magnetizations.

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1. Introduction

Superparamagnetic colloids improve the contrast in Magnetic Resonance Imaging (MRI). Thanks to their great magnetization, the nanoparticles induce great variations in the surrounding water-proton relaxation times.

Among many possible materials for fabrication of magnetic nanoparticles [1] iron oxide is the most promising since it is non-toxic, and fabrication of nanoparticles does not require hazardous organic solvents and extreme conditions of pressure or temperature [2,3]. Iron oxide nanoparticles (NPs) predominantly shorten T_2 transverse relaxation time and thus provide negative contrast in T_2 weighted images. Moreover, iron oxide NPs can easily be coated by protective layers enhancing their colloidal stability and biocompatibility.

The T_2 relaxation time depends on many parameters of the NPs, therefore their function as contrast agents is also a function of those parameters. Thus, a careful analysis of those parameters allows for recognizing optimal ranges of their values and designing synthesis procedures leading to possibly best outcomes. The decrease in T_2 has been explained theoretically for single spherical NPs by the inner- and outer-sphere theory [4], then refined with chemical exchange [4,5] and partial refocusing models [6]. When theoretical models became invalid, particularly for analysis of NPs agglomerates, computational methods were employed. Those methods were based on a simple random walk scheme for water-protons motion while NPs were normally static. Also, no intermolecular interactions (except of hard-core repulsion) were taken into account [6–10]. Though simple, the random walk methods allowed drawing very useful conclusions concerning the NPs sizes, agglomeration, cluster sizes and structure in the modification of the transverse relaxation times.

The aim of this work is the analysis of various parameters of magnetic NPs in the modification of T_2 relaxation time but we focus on possibly a complete description of intermolecular interactions and the dynamics of motion of both water-protons and magnetic nanoparticles. For that purpose we designed a full molecular

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dynamics model of the NPs suspension in aqueous media accounting for dispersion forces, electrostatic interactions and magnetic interactions including magnetization reversal within the nanoparticle volume. All those factors are carefully studied and conclusions concerning their meaning are provided.

Our calculations cover the range of parameters representative of chitosan covered iron oxide nanoparticles. Those NPs have recently been synthesized and characterized in our group [3]. It was found that they form highly stable and biocompatible suspensions; moreover, they reveal very high relaxivity values. Thus, another aim of this work is devoted to theoretical understanding of the observed properties of chitosan covered nanoparticles and finding possible routes for optimization of their properties.

2. Methods

All calculations were performed using the Large-scale Atomic/Molecular Massively Parallel Simulator (lammps) code [11] with several extra classes written from scratch and working on magnetic torques. The force field consisted of several interactions types which are shortly discussed in subsequent paragraphs.

2.1. Magnetic Interactions

A superparamagnetic nanoparticle is modeled as a sphere of radius $r = r_M + \delta$, that is, it is composed of a magnetic core of radius r_M and nonmagnetic shell of thickness δ. The magnetic core is characterized by some value of the saturation magnetization M_s, thus the particle magnetization

$$\vec{m} = M_s V[m_x, m_y, m_z] \tag{1}$$

where m_i are unit vectors of magnetization and $V = (4/3)\pi r_M^3$. Each NP has also an easy axis of magnetization $\vec{e}$ which defines an equilibrium direction of magnetization. In the absence of external magnetic field the magnetization aligns with the direction of the easy axis and any displacement of the magnetization is accompanied by the anisotropy energy increase

$$E_a = K_a \sin^2\theta \tag{2}$$

where $\cos\theta = \vec{m}\cdot\vec{e}$ and K_a is the magnetic anisotropy constant. Thus, any displacement of magnetization orientation induces the anisotropy torque $\vec{\tau}_a$ acting on the magnetization vector

$$\vec{\tau}_a = \vec{m}\times\vec{\nabla}E_a \tag{3}$$

The same torque but of opposite direction acts on the easy axis vector.

The presence of other magnetic NPs and external magnetic field, B, induce magnetic torques due to dipole–dipole interactions $\vec{\tau}_d$ and dipole–field interactions $\vec{\tau}_B$. The dipole–dipole interactions can be adequately described by the Dormann–Bessais–Fiorani model [12] which yields the following formula for dipole–dipole torque

$$\vec{\tau}_d = \frac{\mu_0}{4\pi}\left[\frac{3(\vec{m}_i\cdot\vec{d})(\vec{m}_j\times\vec{d})}{d^5} - \frac{\vec{m}_i\times\vec{m}_j}{d^3}\right] \tag{4}$$

where μ_0 is the magnetic permeability of free space and d is the distance between two dipoles. The dipole–field interaction leads to $\vec{\tau}_B$ torque acting on the dipole

$$\vec{\tau}_B = \vec{m}\times\vec{B} \tag{5}$$

where B is the external magnetic flux density.

The sum of the above contributions drives the Néel rotation (rotation of the magnetic moment between easy axes) of the NP magnetization, however, due to the coupling in Eq. (3) the Brownian rotation (rotation of the NP as a whole within its body frame) occurs as well, that is

$$\frac{d\vec{\omega}_{NP}}{dt} = -I^{-1}\vec{\tau}_a \tag{6}$$

where I is the NP inertia. As seen, the Eq. (6) defines the angular acceleration of the Brownian rotation. It is driven by the magnetic anisotropy torque only and it is calculated from Eq. (3). The negative sign means that the direction of the torque acting on the easy axis is opposite to the torque acting on the magnetization vector.

The instantaneous orientation of the easy axis can be found by integration of the following equation

$$\frac{d\vec{e}}{dt} = \vec{\omega}_{NP}\times\vec{e} \tag{7}$$

In the case of fine magnetic nanoparticles revealing moderate anisotropy constants the inertialess Néel rotation is much faster than the Brownian rotation. Thus, the full description of the dynamics of magnetization reversal according to the Landau–Lifshitz–Gilbert equation [13,14] is not necessary and we may rely only on its stationary solution. That solution has been found by analyzing the Fokker–Planck equation governing the time evolution of the nonequilibrium probability distribution of magnetic moments orientations associated with the stochastic Landau–Lifshitz–Gilbert equation [13]. Thus, on introducing the appropriate Néel time t_0, which is the characteristic time of free diffusion in the absence of potential, the stationary solution of the Fokker–Planck equation has the Boltzmann distribution when

$$t_0 = \frac{1}{\lambda}\frac{|\vec{m}|}{2\gamma kT} \tag{8}$$

where γ is a gyromagnetic ratio and λ is a dimensionless damping coefficient that measures the magnitude of the relaxation (damping) term relative to the gyromagnetic term in the dynamical equation. We can further assume that magnetization reversal proceeds according to a coherent rotation mechanism, that is, the magnitude of magnetization does not change during rotation of the moment and thermal agitation helps crossing the energy barrier associated with magnetic anisotropy (Néel–Brown model). That mechanism has been experimentally confirmed for the case of cobalt and some other nanoparticles [15]. So, the magnetization reversal is in our case a simple free rotational diffusion process with an activation barrier. Thus, a mean time spent at a given orientation t_N follows the exponential law,

$$t_N = t_0\exp(E/kT) \tag{9}$$

where E is the net activation barrier,

$$E = K_a V\sin^2\theta - \vec{m}\cdot\vec{B}\,. \tag{10}$$

Eq. (10) shows that the barrier for rotational diffusion is controlled mainly by the magnetic anisotropy energy and the energy of magnetic dipole in the external field. Formally, it also depends on the dipole–dipole energy but that component is negligible in our case.

The dynamics of inertialess magnetization reversal of the magnetic moments is therefore described by the overdamped Langevin dynamics. According to that scheme the angular acceleration is zero because all forces (torques) and friction terms are compensated by stochastic terms and the motion becomes inertialess. It physically means that the Néel rotation becomes a simple rotational diffusion process. Under the above assumptions the angular velocity of magnetization $\vec{\omega}_m$ reads,

$$\vec{\omega}_m = \frac{\lambda\gamma}{M_s V}\vec{\tau}_m + \vec{\omega}_{NP} + \sqrt{\frac{2\lambda\gamma kT}{M_s V\Delta t}}\vec{R} \tag{11}$$

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