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Physical aspects of magnetic hyperthermia: Low-frequency ac field absorption in a magnetic colloid

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ABSTRACT

A uniaxially anisotropic superparamagnetic particle suspended in a viscous fluid and subjected to an ac field is considered. Consistently taking into account both internal (Néel) and external (Brownian) magnetic relaxations, a simple expression for the dynamic susceptibility is obtained. This result, with regard to the ac field energy absorption, is compared to the common heuristic approach. This is done for a model polydisperse colloid containing maghemite nanoparticles, which are assumed to posses either bulk or surface magnetic anisotropy. It is shown that viscous losses caused by the particle motion in a fluid matrix make important contribution to the full magnetic response of a ferrocolloid and, thus, its ability to absorb the ac field energy. The obtained exact expression, which takes in both dissipation mechanisms, paves the way to correct optimization of the nanoparticle-mediated heating effect.

1. Introduction

Nowadays, the magneto-inductive hyperthermia is a point of strong interest in the applied physics of magnetic phenomena, see Refs. [1–4] as just few examples. The number of theoretical and, especially, experimental works is growing rapidly inspired by premonition that this method is on the edge of being launched into medical practice. To this essentially multi-disciplinary problem, physics contributes the fundamental part: explains and describes the heating mediated by embedded single-domain particles. Such a particle, whose magnetic moment $\boldsymbol{\mu}$ has a constant length, dissipates the energy of the applied ac field via two channels. Perturbing the Zeeman energy, the field makes $\boldsymbol{\mu}$ to rotate inside the particle. The heat generated by internal friction is transferred outside by way of thermal conductivity. On the other hand, owing to the orientation-dependent anisotropy (bulk, surface and shape), the magnetic moment is coupled to the particle body. In result, the internal motions of $\boldsymbol{\mu}$ induce the particle rotations with respect to the matrix. This motion generates a flow (or deformation) around the particle, so that viscous dissipation heats the matrix directly.

Therefore, to evaluate the total energy absorption, one has to consider two coupled orientational modes: the internal magnetodynamics of $\boldsymbol{\mu}$ and the rotations of the particle. Besides possessing a regular (forced) component, each mode is strongly affected by its own thermofluctuational background, since the reference energies (Zeeman, anisotropy, etc.) are comparable to k_BT. In other words, one faces a problem of multi-dimensional forced rotary Brownian motion, which in the full statement turns out to be rather complicated. Because of that, in the past, the investigations were mostly focused on two limiting cases. The first assumes that the matrix is solid, i.e., the particle body is fixed, so that the only source of the energy absorption and, thus, heating, is the internal mode. In the second limit the particle magnetic anisotropy is set infinite that eliminates the internal magnetodynamics and reduces the problem to the motion of a permanent nanomagnet in a medium with a given rheological behavior, viscous or viscoelastic. Each of these approaches gave birth to a vast literature and by now is quite developed. A good part of the intra-particle magnetodynamic theory is systematized in the book [5]. As to the forced orientational Brownian motion in disparate fluids or elastic matrices, some fundamentals are given in [6–11]. We note that both limiting models have proven themselves quite fruitful and have been confirmed in laboratory experiments, provided the conditions were set in compliance with the model requirements [12–14].

A consistent kinetic equation accounting for the joint motion of a single-domain particle and its magnetic moment was derived in Refs. [15,16]. However, until now there is no comprehensive description enabling one to easily compare the exact theory with the approximate ones, thus establishing justified limits for those.

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The complete model should allow for considering a polydisperse particle assembly. This is important due to the following. Since long ago, there exists a heuristic way to take into account the combined magnetic relaxation in a single-domain particle. As far as we know, Shliomis [17] was the first to propose to characterize the joint process by the relation

$$\tau = \tau_N \tau_B/(\tau_N + \tau_B), \tag{1}$$

where τ_N and τ_B are, respectively, the reference relaxation times of internal and external modes of the magnetic moment. Therefore, this phenomenological formula assigns the main role to the faster process. Eq. (1) remains clear as long as a hypothetical monodisperse assembly is considered. Meanwhile, since the internal (Néel) time exponentially depends on the particle volume, in a typical polydisperse system the ratios τ_N/τ_B for different particles spread both sides of unity.

Besides the magnetic hyperthermia context, a combined description allowing for proper size averaging, is equally necessary for completing the theories for two modern analytical methods. One is magnetic relaxometry. There, functionalized nanoparticles are admixed to the tested solution, and, after incubation, the dynamic magnetic susceptibility of the sample is measured. From these data the enhancement of the particle "hydrodynamic" volume is extracted and, by that, the amount of the adsorbed specific analyte is detected [18–20]. Note that customary materials for the nanoparticles are ferrites: maghemite or magnetite. They are but weakly ansisotropic, and, due to that, quite poorly resemble permanent nanomagnets. This means that to adequately describe the relaxometry measurements one needs to take into account both modes of the rotary motion of the particle magnetic moment. In magneto-optical variant of the relaxometry test, the field-induced birefringence is employed, see Ref. [21], for example. Again, the nanoparticles are admixed to the tested solution. Meeting the sought for molecules, they react and form biomagnetic complexes, sometimes binding several particles together. This modifies the particle size distribution, and, through that, causes substantial changes of intensity and relaxation time of the birefringence signal. To be precise, we remark that the relaxation time governing the kinetics of birefringence in a colloid, although being the same "mechanical" origin, differs from that for the magnetization [6,22].

Another technique, where a detailed description of the particle magneto-orientational kinetics is an essential issue, is the particle-aided contrast in MRI. The effect is based on the change of proton relaxivity in the loci, where magnetic nanoparticles accumulate, e.g. in result of their vectorization against a given pathology. The pertinent characteristic here is the autocorrelation function of the magnetic moment, which certainly comprises the contributions from orientational fluctuations of both the internal and external degrees of freedom [23,24].

This paper is organized as follows. In Section 2 the exact model of the nanoparticle magnetic response to an ac field and the most relevant results on the subject are presented. We restrict the consideration by adopting (*i*) the linear response theory and (*ii*) the low-frequency approximation, which means that the ac field frequency is well below the inverse time τ_D of internal magnetic diffusion, see (6). In Section 3 the behavior of the dynamic magnetic susceptibility is analyzed and illustrated for a typical maghemite sample. In Section 4 the ac field energy absorption, i.e., hyperthermia, is discussed, and predictions of the exact model are compared with those of heuristic models.

2. Joint kinetics of the magnetic moment

Consider a nanoparticle embedded in a nonmagnetic matrix. The particle is single-domain, so that its magnetization M_s is uniform over its volume v_m. For temperatures well below the Curie point, the particle magnetic moment may be presented as $\boldsymbol{\mu} = M_s v_m \boldsymbol{e}$, where $\boldsymbol{e}$ is unit vector, i.e., the direction of $\boldsymbol{\mu}$. In what follows we distinguish between the volume v_m of the magnetic particle and v, its "hydrodynamic" volume that takes into account the surfactant layer of thickness $l_s = 2$ nm, so that $v = (\pi/6)(d + 2l_s)^3$. The latter is used for evaluation of the "hydrodynamic" properties of a particle like the Brownian diffusion time, see Eq. (17) below.

The particle magnetic anisotropy is assumed to be uniaxial with the energy E_A and the easy axis direction determined by unit vector $\boldsymbol{n}$. Then the orientation-dependent part of the particle energy U and the equilibrium distribution function depending on $\boldsymbol{e}$ and $\boldsymbol{n}$ are written as

$$U = -E_A(\boldsymbol{en})^2 - M_s v_m(\boldsymbol{eH}), \tag{2}$$

$$W_0 = Z^{-1} \exp[\sigma(\boldsymbol{en})^2 + \xi(\boldsymbol{eh})], \tag{3}$$

$$Z = \iint \exp[\sigma(\boldsymbol{en})^2 + \xi(\boldsymbol{eh})]\, \mathrm{d}^2\boldsymbol{e}\, \mathrm{d}^2\boldsymbol{n}, \tag{4}$$

where

$$\sigma = E_A/kT, \quad \xi = \mu H/kT, \tag{5}$$

are dimensionless parameters, and $\boldsymbol{h}$ is the unit vector of external magnetic field.

Basically, the difference between the magnetic susceptibilities of the same particle in a solid or liquid environment is due to the difference in the available configuration space. For a particle in a solid matrix only the rotations of vector $\boldsymbol{e}$ are allowed, whereas in a liquid matrix the configuration space comprises two orientational manifolds: $\boldsymbol{e} \otimes \boldsymbol{n}$. In the partition function Z (4) the presence of mechanical degrees of freedom is indicated by integration over $\boldsymbol{n}$. For a trapped particle (solid matrix) in Z only integration over $\boldsymbol{e}$ is retained with $\boldsymbol{n}$ being a parameter. The averaging over the latter, when necessary, is applied to obtain the free energy $F \propto -\overline{\ln Z}$ of a solid assembly, e.g. a randomly oriented system, where the distribution function is angle-independent.

2.1. Particle in a solid matrix

First we consider a mechanically fixed particle. Its internal diffusion modes split into two types—*intrawell* and *interwell*—with regard to the double-well orientational potential imposed by the magnetic anisotropy, see the first term in Eq. (2). According to the magnetodynamic Landau–Lifshitz equation, at zero temperature the response time of the magnetic moment is of the order of precession damping time $\tau_0 = \mu/2\alpha\gamma E_A$, were α is the spin-lattice relaxation parameter and γ is gyromagnetic ratio. Normally, α ranges 0.01–0.1 and is believed to be weakly temperature dependent. The intrawell modes make a countable set, the reference time for all of them is

$$\tau_D = \sigma\tau_0. \tag{6}$$

Note that if the particle volume is constant, parameter σ defined in (5) plays the role of inverse dimensionless temperature.

The interwell mode is always single, and its reference time $\tau(\sigma)$ changes virtually unboundedly in a relatively narrow temperature interval. Qualitatively, the behavior of $\tau(\sigma)$ is as follows. For low potential barriers ($\sigma \ll 1$), the interwell time is close to τ_D, but it grows drastically with σ, and at $\sigma \gg 1$ it is very close to the Néel asymptotic expression $\tau_N = \tau_0 \exp(\sigma)$.

Rigorous description of the motion of $\boldsymbol{e}$ at arbitrary σ is done in terms of a time-dependent orientational distribution function $W(t)$ governed by the rotary diffusion (Brown) equation [25]:

$$\frac{\partial}{\partial t} W = \frac{1}{2\tau_D} \hat{\boldsymbol{J}}_e W \hat{\boldsymbol{J}}_e (U/kT + \ln W); \tag{7}$$

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