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# Optimum size of nanorods for heating application

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ABSTRACT

Magnetic nanoparticles (MNP's) have become increasingly important in heating applications such as hyperthermia treatment of cancer due to their ability to release heat when a remote external alternating magnetic field is applied. It has been shown that the heating capability of such particles varies significantly with the size of particles used. In this paper, we theoretically evaluate the heating capability of rod-shaped MNP's and identify conditions under which these particles display highest efficiency. For optimally sized monodisperse particles, the power generated by rod-shaped particles is found to be equal to that generated by spherical particles. However, for particles which are not mono dispersed, rod-shaped particles are found to be more effective in heating as a result of the greater spread in the power density distribution curve. Additionally, for rod-shaped particles, a dispersion in the radius of the particle contributes more to the reduction in loss power when compared to a dispersion in the length. We further identify the optimum size, i.e the radius and length of nanorods, given a bi-variate log-normal distribution of particle size in two dimensions.



## 1. Introduction

A fascination for the study of MNP's arose due to the potential benefits of their small size coupled with their intrinsic magnetic properties. The synthesis of a cobalt cluster of nanoparticles was first reported in 1995 [1]. Following this, several groups synthesized both isotropic [2] and anisotropic nanoparticles [3,4] through a variety of methods. The magnetic properties of these particles have also been reported by a range of studies on MNP's and clusters [5].

MNP's have been used in heating applications due to hysteresis and relaxational losses which lead to heat dissipation by these particles when present in suspensions [6]. It has been shown conclusively that under an alternating magnetic field MNP's possess the ability to produce intense heat around a small, localized region [7]. The localized heat generation produced by MNP's has gained considerable importance due to its utility in hyperthermia treatment of cancer [8–11]. The temperature profile produced by such particles when present in tumours has been studied extensively through numerical and analytical techniques [12–14]. Various studies have examined the role of particle size, material of synthesis, frequency and amplitude of the applied magnetic field on the effective loss power produced by the particles [13,15–19].

It has been shown through analytical and experimental work that the size of MNP's critically affects the power generated by them [7,19,20]. For spherical MNP's, an optimum size has been found to exist for which the heat generation per unit volume (loss power density) of the nanoparticle is maximum. This occurs due to the competing nature of the Neel and Brownian relaxation mechanisms of heat generation for nanosized superparamagnetic nanoparticles. The Neel relaxation time increases with decrease in particle size and the Brownian relaxation time decreases with decrease in particle size [21–23]. This occurs because Neel losses are governed by switching of spin states in magnetic particles, which is primarily exhibited by smaller sized MNP's while Brownian relaxation occurs due to physical rotation of nanoparticles in the fluid and is enhanced for larger sized MNP's.

In this paper, we focus our attention on rod-shaped particles where the loss power would be determined primarily through relaxational losses. In the past, the use of anisotropic particles for hyperthermia application has been limited by the suggestion that a high magnetic field is necessary to completely utilize the magnetic hysteresis loop of such particles [22]. However, such hysteresis heat loss is expected only for larger sized nanorods, and relaxational losses are expected for nanorods in a smaller size range. Our analysis has been carried out as a result of experimental work on the heating effects of anisotropic nanoparticles which highlights a potential use of such particles in hyperthermia treatment [20,24–26]. Further, we extend the theoretical understanding of heat generation to anisotropic MNP's and show that the maximum power density produced by optimally sized monodisperse rod-shaped and spherical-shaped nanoparticles is equal.

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Additionally, we find that when these differently shaped particles are compared across a similar size distribution, the power generated by nanorods is dramatically enhanced as compared to that by spherical particles. The larger heat generation by rod-shaped particles compared to spherical particles when both are present as a distribution in a solution presents a potential advantage for the use of rod-shaped MNP's in hyperthermia treatment by reducing the dosage of material necessary. The use of anisotropic particles also presents a larger surface area for transfer of agents into the cell, thus allowing for the use of MNP's as better drug delivering agents in the treatment of hyperthermia.

## 2. General formulation

### 2.1. Heat generation through relaxational losses

In our study, we focus our attention on the heat generated by nanoparticles through relaxational losses and ignore the losses due to hysteresis. For small sized nanoparticles, heat loss is governed mainly by two relaxation mechanisms: Neel relaxation and Brownian relaxation. Neel relaxation occurs due to flipping of the orientation of the domain magnetic moment of nanoparticles with respect to the external field in a finite time, known as the Neel relaxation time ($\tau_n$). In the Brownian relaxation mechanism, heat is generated by the rotation of the entire particle in the magnetic field, through Brownian rotation of particles. The mean time for a finite rotation of the particle is known as the Brownian relaxation time ($\tau_b$). Heat loss for smaller sized MNP's is predominantly through Neel relaxation while for larger sized MNP's, heat loss primarily occurs through Brownian relaxational cycles. For MNP's, the heat generated by these two mechanisms occurs simultaneously and therefore, the overall time constant for heat generation is given by [22]

$$\tau^{-1} = \tau_b^{-1} + \tau_n^{-1}, \text{ where} \tag{1}$$

$$\tau_b = \frac{1}{2D_r} \quad \text{and} \quad \tau_n = \frac{\sqrt{\pi}\tau_0 \exp \Gamma}{2\sqrt{\Gamma}}. \tag{2}$$

Here $\tau_0$ is the characteristic relaxation time, which is a property of the magnetic material and $\Gamma = KV_m/k_bT$ is a measure of the anisotropic energy of these particles compared to their thermal energy. $k_b$ is the Boltzmann constant, $T$ is the temperature of the solution and $K$ is the anisotropy constant of the particles, and its effect is enforced later in the section. The Brownian relaxation time ($\tau_b$) is directly proportional to the viscosity ($\eta$) of the medium and thus for highly viscous media, nanoparticles take a longer time to rotate physically. For colloidal particles the diffusivity ($D_r$) is given by $D_r = k_bT/f_r$, through Einstein's formulation, where $f_r$ is the friction factor of the colloidal system.

In this study, the corresponding friction factor of interest is that of Brownian rotation of colloidal particles. Rod-shaped particles have been modeled as prolate ellipsoids, and the friction factor corresponding to axial rotation of particles only is considered due to lower moment of inertia associated with such a rotation compared to the other (around the perpendicular) axis. We define a dimensionless friction factor as $F_r = f_r/8\pi\eta R_e^3$. For spherical particles, $F_r = 1$ and $R_e$ is the radius of the sphere. For rod-shaped nanoparticles [27],

$$F_r = \frac{4(1-q^2)}{3(2-2q^{4/3}/F_t)} \tag{3}$$

$$F_t = \frac{\sqrt{1-q^2}}{q^{2/3}\ln\left(\dfrac{1+\sqrt{1-q^2}}{q}\right)} \tag{4}$$

$$R_e = (lr^2)^{1/3}. \tag{5}$$

Here, $q = 1/a$ where $a$ is the aspect ratio of the rod-shaped particle [defined as the ratio of the diameter of the ellipsoid ($2r$) to the length of the ellipsoid ($2l$)]. Similar expressions described in [27] can be used to estimate the translational friction factor as well as the rotation friction factor about the perpendicular axis.

Based on these expressions, the overall heat generation due to magnetic relaxation losses is given by [22]

$$P = \pi\mu_0\chi_0 H_0^2 f \frac{2\pi f\tau}{1+(2\pi f\tau)^2}. \tag{6}$$

Here, $P$ is the power generated per unit volume of the nanoparticle, $\mu_0$ is the magnetic permeability of free space, $\chi_0$ is the magnetic susceptibility of the material, $H_0$ is the magnitude of the applied field strength, $f$ is the frequency of magnetic oscillations and $\tau$ is the mean relaxation time for the process. From Eq. (6), it is clear that when $f\tau \gg 1$, the power generated by the particles varies linearly with the external frequency of oscillations. When $f\tau \ll 1$, the power generated by the particles tends to 0. It is also evident from the expressions, that the maximum power generated by the nanoparticles occurs when $f = 1/\tau$. Since the power generated is not linearly related to the relaxation time, the overall effect can only be understood when Eq. (6) is studied in conjugation with Eq. (1). The magnetic susceptibility of a nanoparticle ($\chi_0$) is given by [22]

$$\chi_0 = \frac{\mu_0 \phi M_d^2 V_m}{3kT}\frac{3}{\zeta}\left(\coth\zeta - \frac{1}{\zeta}\right). \tag{7}$$

Here, $\phi$ is the volume fraction of the particles in the solution, $M_d$ is the domain magnetization of the particles. $\zeta = \mu_0 M_d H V_m/k_bT$ where $H$ is the magnetic field which has been externally applied on the system. From these expressions, it is evident that the heat generated by MNP's present in a solution is volumetric in nature, and the shape affects both the anisotropic constant ($K$) for the system and the Brownian relaxation time.

Expressions derived above for calculating the heat loss by spherical nanoparticles have been well studied [5]. For rod-shaped particles, the effect of increased anisotropy of the particles is modeled by modifying the anisotropy constant ($K$) of the particles present in the solution. For spherical particles, this constant of the system is solely determined by the anisotropic effect of various crystal plane orientations on the magnetic polarisability in each direction, and this is represented by using an anisotropy constant known as the magneto-crystalline anisotropy constant, denoted by $K_{mag}$. For rod-shaped particles, in addition to the magneto-crystalline anisotropy constant, a shape anisotropy also exists due to its non-symmetric nature, and is denoted by $K_{shape}$. The effect of both these anisotropy constants are combined in an additive manner to determine the overall anisotropy constant for rod-shaped particles, denoted by $K_{overall}$. Thus for rod-shaped particles, $K_{overall} = K_{mag} + K_{shape}$. The experimental study of heat generation by spherical particles can allow us to determine the magneto-crystalline anisotropy constant of the material. This contribution is assumed to be identical for both spherical and rod-shaped particles of the same material. Based on the theory developed by Cullity et al. [28], the shape anisotropy for rod-shaped particles can be estimated by approximating them as prolate spheroids, and is given by

$$K_{shape} = 0.5\mu_0(N_a - N_c)M_s^2. \tag{8}$$

Here, $N_a$ and $N_c$ represent the demagnetization constants for the rod-shaped particles, and are functions of the aspect ratio ($a$). Rod-shaped particles are again modelled as prolate spheroids, and the demagnetization along the two directions have been