Theory of magnetic fluid heating with an alternating magnetic field with temperature dependent materials properties for self-regulated heating

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Magnetic nanoparticles (MNP) offer promise for local hyperthermia, thermoablative cancer therapy and microwave curing of polymers. Rosensweig's theory predicts that particle size dependence on RF magnetic heating of ferrofluids is chiefly determined by magnetic moment, magnetic anisotropy, and the viscosity of the fluid. Since relaxation times are thermally activated and material parameters can have strong T dependences, heating rates peak at a certain temperature. We extend the model to include the T dependence of the magnetization and anisotropy using mean field theory and literature reported T dependences of selected fluids considered for biomedical applications. We model materials with Curie temperatures near room temperature for which the magnetic properties are strongly T dependent to address the problem of self-regulated heating of ferrofluids. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3076043]

I. INTRODUCTION

Magnetic nanoparticles (MNPs) have been considered for biomedical applications for decades.[1–4] Of interest is the use of MNPs as point heat sources in the presence of radio frequency (RF) magnetic fields for hyperthermic cancer treatments. By heating tissues from 42 to 46 °C, cancerous cells can be selectively damaged without much harm to the healthy surrounding tissue.[5,6] Above 42 °C, the cancer cells also become more susceptible to conventional drug treatments.[4,7] Tolerable limits of inductive heating of tissues limit the safe range of magnetic field amplitudes and frequency that can be employed for magnetic hyperthermia therapy (MHT). It has been shown that any combination of field strength (H) and frequency (f) will be biologically noninvasive when $H*f \leq 4.85\times 10^8$ Hz-A/m.[8,9]

During MHT, MNPs dissipate applied magnetic energy through eddy currents, hysteresis, resonance, and relaxation losses. The loss mechanism that dominates depends on the micromagnetics of the switching and the perfection of the crystals. The Rosensweig model considers only relaxation losses. These losses are diminished near the Curie temperature (T_C) of the ferromagnetic material. If the composition of a material, is tuned so that T_C is brought near the desired maximum temperature, the heating can be self-regulating so that the tissues will not overheat.[10]

The heating rate in a ferrofluid is also strongly depends on the saturation magnetization, magnetic anisotropy, and carrier viscosity. In this study, we have extended the Rosensweig's model[2] to incorporate the temperature dependence of material properties for alloys with $T_C \sim 320$ K, which could be of interest in self-regulated MHT applications.

II. THEORY OF RELAXATION PROCESS IN MAGNETIC FLUID

In MHT, superparamagnetic nanoparticles dispersed in a ferrofluid are introduced into the tumor and subjected to a nonbioinvasive RF field to eliminate cancer cells. AC magnetic fields cause the magnetization vector to repeatedly relax and to release heat. Brown and Néel relaxations are the dominant means of power dissipation. Brown relaxation occurs when a nanoparticle rotates through the medium, resulting in heat dissipation through frictional interaction between the particle and its surrounding medium. Néel relaxation occurs when the MNP remains stationary and the moment rotates within the crystal. These modes have a characteristic Brown and Néel relaxation times are given by[1,2]

$$\tau_B = \frac{3\eta V_H}{k_B T}, \quad \tau_N = \frac{\frac{\sqrt{\pi}}{2\tau_0} e^{\frac{KV_M}{k_B T}}}{\sqrt{\frac{KV_M}{k_B T}}}, \tag{1}$$

which is dependent on both the viscosity of the medium as well as the hydrodynamic volume V_H, while V_M is the magnetic volume of the nanoparticle and K, is the anisotropy constant. Brown relaxation times are approximately 10^3 times larger than Néel relaxation times in mediums with large viscosities such as living tissue.[11–13]

A general anisotropy can be written as[14]

$$K^{\text{eff}} = K^v + \frac{K^s}{d}. \tag{2}$$

The volume anisotropy term, K^v, contains the magnetocrystalline, shape, and other anisotropies. The surface term, K^s, has a linear dependence on the radius of the particle and will be scaled by an appropriate shape factor (three for spheres).

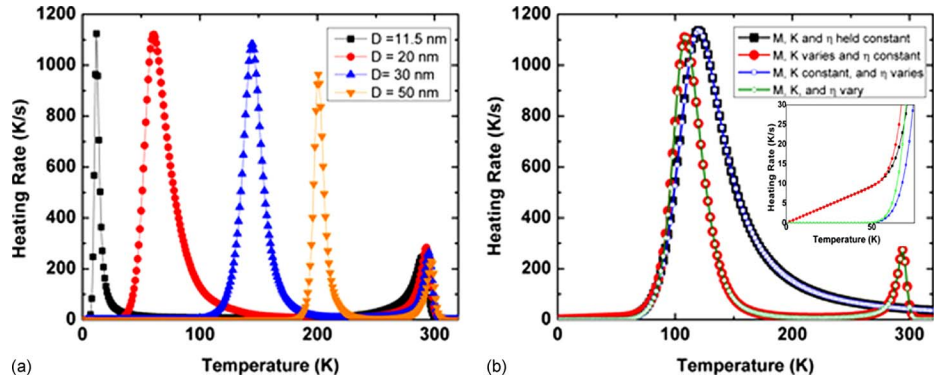

FIG. 1. (Color online) Graphical representation of MATHEMATICA modeling demonstrating the effect of temperature dependence on the heating parameters of viscosity, anisotropy, and magnetization. (a) Heating rate of monodisperse nanoparticles of varying size with respect to temperature with all parameters sensitive to temperature. (b) Heating rate peak of monodisperse 25 nm particles with parameters sensitive to temperature.

Because of the small particle sizes, this can be a significant term.

Although power dissipation is dependent on many variables, particle size is among the most influential. A limitation is placed that the MNP size should be no larger than ~15 nm to allow their colloidal suspension and to ensure superparamagnetic behavior. This paper illustrate results for particles with larger sizes for the purpose of visualization of the size effect on heating.

III. THEORY OF RF HEATING WITH *T*-DEPENDENT MATERIAL PARAMATERS

We consider Néel and Brown relaxation processes to occur in parallel, with relaxation time τ_R:

$$\frac{1}{\tau_R} = \frac{1}{\tau_N} + \frac{1}{\tau_B}. \tag{3}$$

The relaxation results in a volumetric power dissipation in an RF field of amplitude H and frequency f:

$$P = \pi\mu_0\chi''H^2 f, \tag{4}$$

where μ_0 is the permeability of free space and χ'' is the imaginary part of the complex magnetic susceptibility, χ. The magnetic susceptibility, loss component, and static susceptibility for exponential relaxation with a time constant τ and angular frequency $\omega=2\pi f$ are

$$\chi = \frac{\chi_0}{(1+i\varpi\tau)}, \quad \chi'' = \frac{\varpi\tau}{1+(\varpi\tau)^2}\chi_0, \quad \chi_0 = \chi_i\frac{3}{\xi}\left(\coth\xi - \frac{1}{\xi}\right), \tag{5}$$

where ξ, the Langevin parameter, and χ_i, the initial susceptibility, are given by:

$$\xi = \frac{\mu_0 M_d H V_M}{k_B T}, \quad \chi_i = \frac{\mu_0 M_d^2 V_M}{3k_B T}, \tag{6}$$

where M_d is the domain magnetization of MNP. In this work, we consider monodisperse MNPs. The heat from the relaxation losses leads to a rate of temperature rise given by

$$\frac{\Delta T}{\Delta t} = \frac{P}{\rho c_p}, \tag{7}$$

where ρ is the weighted density and c_p is the weighted specific heat capacity of the system considering the MNP concentration, φ, within the carrier medium.

Our previous mathematical models[1]: predict the losses due to RF fields, with material parameters remaining constant throughout the heating process. However, viscosity, anisotropy, and magnetization have strong temperature dependences. Therefore, we extend the previous model, taking into consideration the temperature dependence of the material properties to predict their effect on heating rates. The viscosity T dependence in our model is accounted for by using experimental measurements of aqueous polyethylene fitted with a modified Eyring's viscosity model for polymer-solvent mixtures.[15] The T dependence of magnetization was determined using mean field theory.[16] The T dependence of the magnetic anisotropy was treated using Akulov's theory.[17]

The T dependence of the magnetization is treated within the classical Langevin theory,[14] where the magnetization decrease from the saturation magnetization to zero at T_C:

$$M = M_0 \tanh\left[\left(\frac{M_s(T)}{M_0}\right)\left(\frac{T_c}{T}\right)\right], \tag{8}$$

where M_0 is the 0 K saturation magnetization. Anisotropy has a strong T dependence which is expressed as a power law of the reduced magnetization, $m(T)=M_s(T)/M_s(0)$, of the form $K=K_0 m(T)^{n(n+1)/2}$. n is the lowest order spherical harmonics in the anisotropy expansion. According to Akulov's theory,[17] icosahedral materials, $n=6$, have an anisotropic temperature dependence of $K=[m(T)]^{21}$ cubic materials, $n=4$, can be written as $K=[m(T)]^{10}$, and uniaxial materials, $n=2$, have an anisotropy of $K=[m(T)]^3$. The steep power laws indicate that the magnetic anisotropy will decrease faster than magnetization with increasing T.

Aqueous solution of a typical biocompatible polymeric surfactant, polyethylene glycol (PEG) with 10 kg/mol molecular weight was considered as the carrier fluid. A modified Eyring viscosity model was used for a binary mixture of PEG and water.[15]

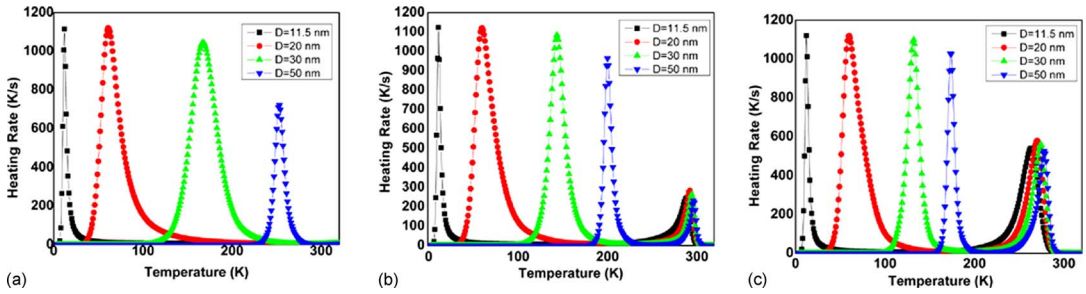

FIG. 2. (Color online) Graphic representation of MATHEMATICA modeling demonstrating the effect on heating rate of varying symmetry within the particles. (a) Uniaxial material with $K=[m(T)]^3$, (b) cubic material with $K=[m(T)]^{10}$, and (c) icosahedral material with $K=[m(T)]^{21}$.

IV. RESULTS AND DISCUSSION

Figure 1(a) shows the T dependence of the heating rate for several MNP particle sizes for a model system. We chose a theoretical alloy with $M_s=116$ kA/m, $T_C=300$ K, and an anisotropy value of 1500 kJ/m^3, encapsulated in aqueous PEG. Theoretical heating rates were determined using MATHEMATICA® code implementation of the theory in the prior section. The theoretical heating parameters used were a field of 50 mT and a frequency of 300 kHz. The strongly size-dependent heating rate, peaked at particular temperatures, indicates the importance of particle size in tuning the heating rate peak to temperatures dictated by applications.

Figure 1(a) shows a previously unpredicted peak in the heating rate to occur near T_C. This peak is reminiscent of a Hopkinson peak, which occurs due to a more rapid decrease in the magnetization than that of magnetic anisotropy as the temperature approaches T_C. This causes the magnetic permeability to diverge[18] which causes a peak in heating. This peak is relatively independent of particle size. This heating is comparable to other materials used for hyperthermia treatments such as iron oxides. This peak can be tuned depending on the material's T_C. This heating can self-regulate, and cease once a particular temperature is reached, and can be achieved with polydisperse nanoparticles.

Figure 1(b) considers the relative importance of the temperature variation in the viscosity, magnetic anisotropy, and magnetization. When magnetization and anisotropy values are fixed, the heating rate is higher than it would be with realistic T dependences. At low T, the importance of the temperature dependence of viscosity is seen. Here the value for viscosity is high and prevents the Brownian mode of heating. The Hopkinson peak occurs only when the anisotropy and magnetization T dependence is included due to the faster decrease in magnetization values as compared to anisotropy.

Figure 2 shows the role of the T dependence of the anisotropy. Figure 2(a) shows the heating rates of a uniaxial material with $K=[m(T)]^3$, Fig. 2(b) is a cubic material with $K=[m(T)]^{10}$, and Fig. 2(c) is an icosahedral material with $K=[m(T)]^{21}$. Uniaxial materials do not show a significant Hopkinson peak (because the T dependence of anisotropy decreases at a slower rate than for cubic and icosahedral materials).

V. CONCLUSION

A suitable alloy with high saturation magnetization and a T_C that is tuned to a particular temperature, by changing composition, will have interesting biomedical applications such as hyperthermic cancer treatments or polymer/epoxy curing. Having a system that is self-regulating, or stops heating at a particular temperature, would be useful to prevent excess heating that could damage healthy tissues or the epoxy, respectively. This promotes safety and assurance that other tissues will not be harmed during treatment.

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