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Electronic Supplementary Information

Temperature-dependent heating efficiency of magnetic nanoparticles for applications in precision nanomedicine

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I. RATE EQUATIONS

Magnetic nanoparticles (NPs) with predominant uniaxial anisotropy can be described as double-well systems (DWS). The model is exploited to draw and analyze the hysteresis loops of particles submitted to cyclic magnetization. Here, the main assumptions laeding to the rate equations are given.

Each magnetic nanoparticle has size D, effective volume $V = (\pi/6)D^3$ and magnetic moment $\mu = M_s V$ where M_s is the saturation magnetization of the material; in the absence of magnetic field, the magnetic moment is aligned by to the easy axis by uniaxial anisotropy of amplitude K_{eff} The easy directions of NPs are assumed to be evenly distributed in space; in Figure 1 the plane containing the rotation of the μ vector is defined by the applied field H and the easy axis of a nanoparticle.

Let N_ϕ be the number (per unit volume) of particles of magnetic moment μ whose easy axis forms an angle ϕ with respect to H. For easy-axis directions evenly distributed in space, $N_\phi = N/2\pi$, N being the total number (per unit volume) of particles in the system. For each angle ϕ the occupancy numbers in the two wells are $N_{1\phi}$ and $N_{2\phi}$ ($N_{1\phi}+N_{2\phi} = N_\phi$).

The energy of a single DWS, $E(\theta, \phi)$ is:

$$E(\theta, \phi) = K_{eff}(T)Vsin^2(\theta) - 2HM_s(T)Vcos(\theta - \phi)$$

where θ is the angle between the magnetic moment direction and the easy axis. The angles

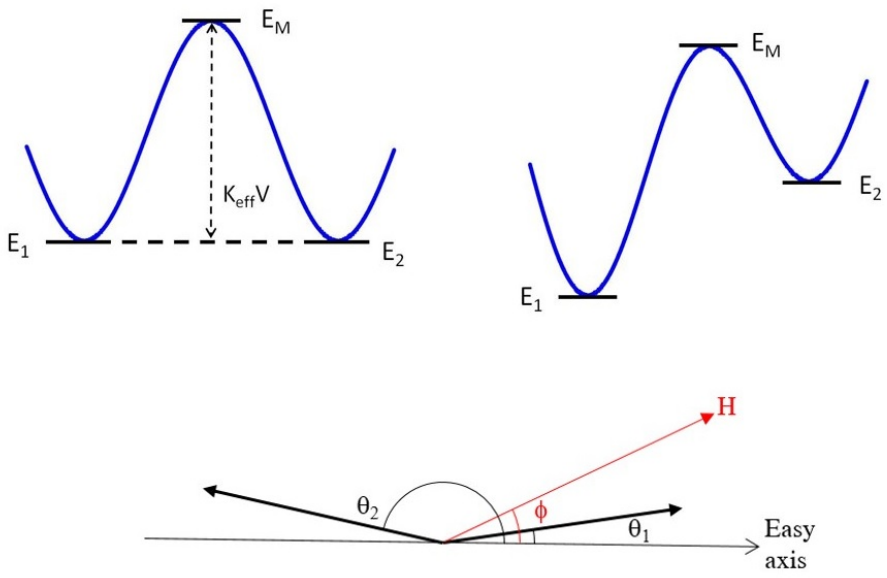

FIG. 1. Top: energy of the DWS without and with applied field; bottom: reference system (easy axis parallel to the x-axis).

of minimum energy $\theta_1(\phi)$, $\theta_2(\phi)$ (see Figure 1) are found by requiring that the derivative of $E(\theta, \phi)$ with respect to θ be equal to zero; the magnetization along the field direction at the temperature T is therefore:

$$M(T,\phi) = N_{1\phi}(T)M_s(T)Vcos(\theta_1(\phi) - \phi) \\ +N_{2\phi}(T)M_s(T)Vcos(\theta_2(\phi) - \phi).$$

The redistribution of particles in the two wells is ruled by the rate equations:

$$\frac{dN_{1\phi}}{dt} = -\frac{1}{\tau_1(t)}N_{1\phi} + \frac{1}{\tau_2(t)}N_{2\phi} = \frac{N_\phi}{\tau_2(t)} - \Big(\frac{1}{\tau_1(t)} + \frac{1}{\tau_2(t)}\Big)N_{1\phi} \\ \frac{dN_{2\phi}}{dt} = \frac{1}{\tau_1(t)}N_{1\phi} - \frac{1}{\tau_2(t)}N_{2\phi} = \frac{N_\phi}{\tau_1(t)} - \Big(\frac{1}{\tau_1(t)} + \frac{1}{\tau_2(t)}\Big)N_{2\phi}. \quad (1)$$

In the standard Arrhenius picture the time-dependent escape frequencies are:

$$\tau_i^{-1}(t) = \tau_0^{-1}exp\Big(-\frac{E_M(t) - E_i(t)}{k_BT}\Big) \qquad (i = 1, 2)$$

where $E_i(t)$ are the energies of the two energy minima, $E_M(t)$ is the energy at the top of the barrier(see Figure 1).

The energies $E_{i,M}$ depend on time when $H = H(t)$. The problem's symmetry dictates the general relationship $\tau_1(-H) = \tau_2(H)$ that holds at all angles ϕ.

In high-frequency measurements τ_{meas} is conventionally taken as the reciprocal of measurement frequency. In this case the sweep rate is no longer a constant; nevertheless, it is still possible to introduce a r.m.s sweep rate R_{RMS} defined as $R_{RMS} = (\pi/\sqrt{2})H_v f$ where H_v is the vertex field. The dimensionless rate equations (1) can be rewritten in terms of the magnetic field H:

$$\begin{aligned} \frac{dN_{1,\phi}}{dH} &= \mp\frac{1}{R_{RMS}}\Big[\frac{N_\phi}{\tau_2(h)} - \Big(\frac{1}{\tau_1(h)} + \frac{1}{\tau_2(h)}\Big)N_{1,\phi}\Big] \\ \frac{dN_{2,\phi}}{dH} &= \mp\frac{1}{R_{RMS}}\Big[\frac{N_\phi}{\tau_1(h)} - \Big(\frac{1}{\tau_1(h)} + \frac{1}{\tau_2(h)}\Big)N_{2,\phi}\Big]. \end{aligned} \tag{2}$$

where the $\mp$ sign refers to the upper/lower loop branch.

The behavior of a DWS assembly with randomly distributed easy axes is obtained by averaging the solutions of the full rate equations (2) over all ϕ angles.

In three dimensions, the average of a ϕ-dependent quantity $g(\phi)$ is the sum: $\sum_1^N g(\phi_i)sin(\phi_i)/\sum_1^N sin(\phi_i)$ over N angles in the interval $-\pi/2 \leq \phi_i \leq \pi/2$. In this work, N has been fixed to 181; the relative difference between the average done with $N = 181$ and with $N = 1801$ is negligible ($< 2 \times 10^{-3}$).

II. ON THE VALIDITY OF RATE EQUATIONS

The rate-equation approach is a simplifying approximation to the Fokker-Planck equation for the double-well problem. For magnetic nanoparticles, rate equations naturally emerge from the Fokker-Planck equation when the ratio $K_{eff}V/k_BT$ is significantly larger than unity; therefore the validity of the approach at a given temperature depends on both magnetic anisotropy and nanoparticle size.

In rate equations containing time-dependent escape frequencies, as the ones studied here,

detailed balancing is achieved only when $\omega\tau_c << 1$ where τ_c is the characteristic relaxation time of the system. In magnetic nanoparticles, the free diffusion time of magnetization is $\tau_c = M_s V(1+\alpha^2)/2\gamma\alpha k_B T$ where γ is the electron gyromagnetic ratio and α is the Gilbert's damping constant appropriate to describe systems with intermediate-to-high damping ($\alpha \approx 1$) such as magnetic nanoparticles. Using $\alpha = 0.5$ one gets $\tau_c = 1.06 \times 10^{-9}$ s for $D = 15$ nm. In this case, the driving-field frequency should be much lower than 1.50×10^8 Hz to guarantee detailed balancing. In fact, the driving-field frequency used in the paper ($f = 1 \times 10^5$ Hz) ensures that rate equations can be confidently applied for all studied nanoparticle sizes.