Superparamagnetic Relaxation Times for Mixed Cubic and Uniaxial Anisotropy and High Energy Barriers: II. Intermediate-to-High Damping and Uniaxial Axis in a \{111\} Direction

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Superparamagnetic relaxation rates are calculated for ferromagnetic particles with mixed cubic and uniaxial anisotropy. In Part I the uniaxial axis is in a \{001\} crystallographic direction, while in this article it is in a \{111\} crystallographic direction. The method is a generalization of the uniaxial theory of W. F. Brown, Jr. [Phys. Rev. 130, 1677 (1963)] for high energy barriers and intermediate-to-high dissipation. Relaxation rates are obtained for the distribution of probability among remanent states and the resulting magnetic moment. The magnetic moment can be separated into components parallel to and perpendicular to the uniaxial easy axis with independent relaxation rates. These rates depend on the uniaxial anisotropy parameter \(K_u\) and the cubic anisotropy parameter \(K_1\).

For oblate anisotropies \((K_u < 0)\) the relaxation is nearly isotropic, but as \(K_u\) passes zero a strong anisotropy develops. If \(K'_1 > 0\) and \(0 < K_u < 0.7611K'_1\), the effect of increasing \(K_u\) is to decrease the parallel rate and increase the perpendicular rate. The perpendicular component is identically zero for larger \(K_u\). If \(K'_1 < 0\) and \(0 < K_u < 0.2229|K'_1|\), there are two relaxation rates for the parallel component. One is nearly equal to the perpendicular rate and is an increasing function of \(K_u\) while the other is a decreasing function of \(K_u\). The effect of the more rapid rate is to increase the parallel component to saturation. The parallel component then decays at the slower rate. If a sample has oriented ferromagnetic particles, it can have a superparamagnetic relaxation rate with a strong directional dependence.

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I. INTRODUCTION

In this article and part I\(^1\) of the series (hereafter referred to as N1) I generalized the Néel-Brown theory\(^2,3\) for superparamagnetic relaxation rates. I calculate the superparamagnetic relaxation times for ferromagnets with two anisotropy components, one cubic and one uniaxial. In N1 the easy axis is in a \{001\} crystallographic direction; in this article it is in a \{111\} direction. I assume that energy barriers are high enough to make transitions rare, and the damping is intermediate-to-high. The theory and notation is developed in N1.

II. RESULTS

Below, the same organization is used as in N1. In section II A the equilibrium solutions are calculated as functions of the ratio \(K_u/K'_1\). In section II B the eigenvalues of the Jacobian are calculated for each solution to determine whether the solution is a minimum, maximum or saddle point. The results of section II A and II B are used in section II C to calculate the prefactor for the attempt frequency over each saddle point. In section II D the master equations are constructed and solved to give the time dependence of the probability of each state as a function of the single-barrier frequencies. Finally, the solutions for the probability are used to derive the time dependence of the magnetic moment.

In superparamagnetic and single-domain particles the instantaneous magnetization \(\mathbf{M}\) always has magnitude \(|\mathbf{M}| = M_s\), where \(M_s\) is the saturation magnetization. Equilibrium states are stationary points of the free energy with the constraint \(|\mathbf{M}| = M_s\). The free energy density \(g\) depends on the direction cosines \(\mathbf{M}/M_s = (\alpha, \beta, \gamma)\) of the magnetization and the anisotropy parameters \(K_u\) (uniaxial) and \(K'_1\) (cubic). With the uniaxial axis in the \{111\} direction,

\[
g = K_u \left(1 - (\alpha + \beta + \gamma)^2/3\right) + K'_1(\alpha^2\beta^2 + \beta^2\gamma^2 + \gamma^2\alpha^2).
\]

(1)

The case \(K'_1 = 0\) (pure uniaxial) was treated by Brown\(^4\). Assuming \(K'_1 \neq 0\), let \(\kappa = K_u/K'_1\). The equilibrium solutions can be simplified considerably if we rotate to a coordinate system with \(x, y, z\) axes in the \{110\}, \{112\} and \{111\} directions. The new coordinates \(\mathbf{m} = (\alpha, \beta, \gamma)^T\) are given by \(\mathbf{m} = R^{-1} \cdot \mathbf{t}\), where \(\mathbf{m} = (\alpha, \beta, \gamma)^T\) and

\[
R_{ij} = \begin{pmatrix}
1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\
-1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\
0 & -2/\sqrt{6} & 1/\sqrt{3}
\end{pmatrix}.
\]

(2)

Substituting for \(\mathbf{m}\) in (1), we obtain an expression for \(g\) in the tilde coordinates. This expression is even in \(\tilde{\alpha}\). Substituting \(\tilde{\alpha}^2 = 1 - \tilde{\beta}^2 - \tilde{\gamma}^2\) and taking derivatives with respect to \(\tilde{\beta}\) and \(\tilde{\gamma}\), we obtain the equilibrium equations:

A. Equilibrium States
The equations were derived using symbolic algebra (see the electronic supplement). The solutions of (3a) are \( \gamma = 0 \) and \( \gamma = \pm (1 - 4\beta^2)^{1/2} \). If \( \gamma = 0 \) then \((\alpha, \beta, \gamma) = (\pm 1, 0, 0) \) or \((\pm 1/2, \pm \sqrt{3}/2, 0) \). These six solutions, in crystallographic coordinates, are the \((110) \) directions that are perpendicular to the \([111] \) direction. I will refer to them as the \(110_1\) solutions.

If the other solution of (3a), \( \gamma = \pm (1 - 4\beta^2)^{1/2} \), is substituted in (3b), the result is

\[
2^{1/2} \beta (-3 + 16\beta^2) = \mp \left( 1 - 4\beta^2 \right)^{1/2} (3\kappa - 2 + 14\beta^2). \tag{4}
\]

Squaring both sides leads to a third order equation in \( \beta^2 \):

\[
\beta^6 + r\beta^4 + s\beta^2 + t = 0, \tag{5}
\]

where

\[
r = (28\kappa - 51)/108 \tag{6}
\]

\[
s = (6\kappa^2 - 22\kappa + 15)/216 \tag{7}
\]

\[
t = -(9\kappa^2 - 12\kappa + 4)/1296. \tag{8}
\]

The standard transformation \(^4\)

\[
\tilde{\beta}^2 = x - r/3 \tag{9}
\]

gives the reduced form

\[
x^3 + px + q = 0, \tag{10}
\]

where \( p = (3s - r^2)/3 \) and \( q = 2r^3/27 - rs/3 + t \). In terms of \( \kappa \),

\[
p = (188\kappa^2 - 708\kappa - 171)/34992 \tag{11}
\]

\[
q = -(9436\kappa^3 + 7002\kappa^2 - 621\kappa - 378)/8503056. \tag{12}
\]

The discriminant of (10) is \( D = (p/3)^3 + (q/2)^2 \). If \( D \leq 0 \) there are three real solutions. This is true for \(-0.2229 < \kappa < 0.7611 \). Outside of this range there are two complex conjugates and one real solution.

The solutions of (10) can be expressed in a variety of ways. The following expressions are chosen to ensure that the solutions (and all intermediate steps in calculating the solutions) are always real \(^4\). Let \( R = (\text{sign}(q)) \sqrt{|p|}/3 \). There are three cases:

\( p < 0, \ D \leq 0 \): Let \( \cos \phi = q/(2R^3) \). Then \( x = -2R \cos(\phi/3 + n\pi/3) \) for \( n = 0, 2, 4 \).

\( p < 0, \ D > 0 \): Let \( \cosh \phi = q/(2R^3) \). Then \( x = -2R \cosh(\phi/3) \).

\( p > 0 \): Let \( \sinh \phi = q/(2R^3) \). Then \( x = -2R \sinh(\phi/3) \).

Unfortunately, because of the polynomial dependence of \( p \) and \( q \) on \( \kappa \), the solutions are not smooth functions of \( \kappa \). Jumps between curves occur when \( D = 0 \), or when \( D < 0 \) and either of \( p \) or \( q \) are zero. However, they can be rearranged (see the electronic supplement) to give three smooth solution curves. These curves are shown in Fig. 1.

Although \( \beta^2 \) is always real, \( \beta \) could be imaginary if \( \beta^2 < 0 \). However, the solutions in Fig. 1 appear to be always positive, except perhaps for \( \beta_i^2 \). For the solution to change sign, it must cross zero, which requires that \( t = 0 \) in (5). The only solution for \( t = 0 \) is a double root \( \kappa = 2/3 \). Thus, \( \beta_i^2 \) touches zero but does not cross it.

Below, I will choose \( \beta_i \) to be the negative square root of \( \beta_i^2 \) for \( i = 2 \) and \( \kappa > 2/3 \) and the positive square root otherwise. This ensures that \( \beta_i \) changes smoothly across \( \kappa = 2/3 \) and makes subsequent calculations simpler.

Recall that the equations for \( \beta_i^2 \) were obtained by substituting \( \alpha^2 = 1 - \beta^2 - \gamma^2 \) and \( \gamma = \pm (1 - 4\beta^2)^{1/2} \). With the above conventions for \( \beta_i \), numerical substitutions show that the value of \( \gamma_i \) that solves (3b) is

\[
\gamma_i = s_i \left( 1 - 4\beta_i^2 \right)^{1/2}, \tag{13}
\]

where \( s_i = (1, -1, -1) \). Thus, for each positive root \( \beta_i, i = 1 \ldots 3 \), the equilibrium moments in the tilde coordinate system are

\[
\tilde{m} = \pm \left( \pm \beta_i \sqrt{3}, \beta_i, \gamma_i \right). \tag{14}
\]

Not all the equilibrium states are obtained by the above procedure, but the remainder can be obtained by
appealing to the three-fold symmetry about the \([111]\) axis. The solutions
\[
\mathbf{m} = \pm \left( 0, -2\tilde{\beta}_i, \tilde{\gamma}_i \right).
\tag{15}
\]
are obtained by rotations about this axis. In crystallographic coordinates all the solutions can be written
\[
\mathbf{m} = \pm \left( 2\mathbf{v}^j \tilde{\beta}_j + \mathbf{u} \tilde{\gamma}_j \right),
\tag{16}
\]
where \(\mathbf{u}\) is the unit vector in the \([111]\) direction and \(\mathbf{v}^j\) the unit vector in the \([1\overline{1}2], [2\overline{1}1]\) or \([1\overline{1}2]\) direction. Thus, for each solution \(\tilde{\beta}_i\) there are six directions for the magnetic moment. The energies of these states are
\[
g^{(i)} = \frac{K'_i}{3} \left[ 1 - 8\tilde{\beta}_i^2 + 28\tilde{\beta}_i^4 + 8\sqrt{2}\tilde{\beta}_i^2 \tilde{\gamma}_i^2 + 4K_u\tilde{\beta}_i^4 \right] + \frac{1}{2}K'u\tilde{\gamma}_i^2.
\tag{17}
\]
(See the electronic supplement). When \(K_u = 0\), the solutions are \(\tilde{\beta}_1 = 1/\sqrt{6}, \tilde{\beta}_2 = 1/(2\sqrt{3}),\) and \(\tilde{\beta}_3 = \sqrt{2}/3.\) The corresponding magnetic moments are in the \([001], [1\overline{1}0],\) and \([1\overline{1}1]\) directions (except for \([111]\) and \([\overline{1}1\overline{1}]\)). I will refer to them as the \(g100, g110\) and \(g111\) states (the “\(g\)” stands for “generalized.”).

The other equilibrium solutions for uniaxial axis in the \([111]\) direction are the \([1\overline{1}1]\) and \([\overline{1}1\overline{1}]\) directions, which I will call the \(u\) solutions. These have have energy \(K'_u/3.\) Finally, there are the previously mentioned \(1\overline{1}0\) directions, which have energy \(K_u + K'_u/4.\) All of the solutions are in, or perpendicular to, one of the \((110), (011)\) or \((101)\) planes. The energies of all the states are shown in Fig. 2.

\[\text{FIG. 2: Energies of the equilibrium states normalized by } K'_u.\]

B. Stability

To determine the stability of the states, I use the same approach as in N1, rotating the coordinates so the equilibrium state is in the \(z\) direction and then obtaining the eigenvalues of the Jacobian in the perpendicular coordinates \(x, y.\) Two positive eigenvalues indicate an energy minimum, two negative eigenvalues a maximum, and mixed signs a saddle point. The matrix that maps the crystallographic coordinates onto the new coordinates is the rotation matrix \(R^\perp.\) For the \(u\) state, the tilde coordinates \(\tilde{\alpha}_i, \tilde{\beta}_i\) are perpendicular coordinates, so \(R^\perp\) is given by (2). The eigenvalues of the Jacobian are both equal to \(2K_u - 4K'_u/3.\) Thus, the \(u\) state is an energy minimum for \(K_u > 2K'_u/3\) and a maximum for \(K_u < 2K'_u/3.\)

A suitable rotation matrix for the \(1\overline{1}0\) states is
\[
R^\perp_{ij} = \begin{pmatrix} 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 1/\sqrt{2} & -1/\sqrt{2} \\ 1 & 0 & 0 \end{pmatrix}.
\tag{18}
\]
The resulting eigenvalues are
\[
\lambda_{\pm}/K'_u = -\frac{1}{2} - \kappa \pm \frac{1}{2} \left[ 4\kappa^2 + 4\kappa + 9 \right]^{1/2}.
\tag{19}
\]
This has the form \(a \pm \sqrt{b},\) where \(b - a^2 = 2(K'_u)^2 > 0.\) Therefore, if \(K'_u\) is nonzero, there is always only one positive and one negative eigenvalue, so the \(1\overline{1}0\) states are always saddle points.

For each of the sets of states \(g100, g110\) and \(g111\) we need only determine the stability of one member. It is most convenient to use the state given by (15). Then
\[
\mathbf{m} = \hat{R}^\perp \mathbf{m}^\perp, \quad \text{where}
\]
\[
\hat{R}^\perp_{ij} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \tilde{\gamma}_i & -2\tilde{\beta}_i \\ 0 & 2\tilde{\beta}_i & \tilde{\gamma}_i \end{pmatrix}.
\tag{20}
\]
The matrix that converts crystallographic to perpendicular coordinates is therefore \(R^\perp = R \cdot \hat{R}^\perp.\) Applying this transformation, the eigenvalues for state \(i\) are
\[
\lambda^{(i)}_1/K'_u = \frac{4}{3} \left[ -1 + 11\tilde{\beta}_i^2 - 28\tilde{\beta}_i^4 + 8\sqrt{2}\tilde{\beta}_i^2 \tilde{\gamma}_i^2 + 3\sqrt{2}\tilde{\beta}_i \tilde{\gamma}_i \right] + \kappa(2 - 8\tilde{\beta}_i^2) \tag{21a}
\]
\[
\lambda^{(i)}_2/K'_u = \frac{4}{3} \left[ -1 + 29\tilde{\beta}_i^2 - 112\tilde{\beta}_i^4 + 32\sqrt{2}\tilde{\beta}_i^2 \tilde{\gamma}_i^2 - 3\sqrt{2}\tilde{\beta}_i \tilde{\gamma}_i \right] + \kappa(2 - 16\tilde{\beta}_i^2).
\tag{21b}
\]
The eigenvalues for the three states are plotted in Fig. 3. For \(\kappa < -0.2229\) only the \(g100\) states \((i = 1)\) exist, and they are minima. As \(\kappa\) increases, three transitions occur. At \(\kappa \approx -0.2229\) the \(g100\) and \(g111\) states appear; the \(g110\) state is always a saddle point and the \(g111\) state is a maximum or minimum as \(K'_u > 0\) is positive or negative. The \(g110\) state approaches the \(u\) state as \(\kappa\) increases, meeting it at \(\kappa = 2/3.\) This changes the \(u\) state from minimum to maximum \((K'_u > 0)\) or the reverse \((K'_u < 0).\)
The $g_{110}$ state then moves towards the $g_{100}$ state as $\kappa$ continues to increase. At $\kappa = 0.7611$ the $g_{110}$ and $g_{100}$ states annihilate each other. This leaves the $g_{111}$ state, which is a maximum for $K'_1 > 0$ and a minimum for $K'_1 < 0$.

C. Single-Barrier Relaxation Rates

The equations for the single-barrier relaxation rates $\nu_i$ were developed in N1. Given initial state $i$, final state $j$ and saddle point $s$ in between, the attempt frequency over the saddle point is

$$\nu_{ij} = \nu_{ij}^0 \exp \left[ -(g_s - g_i)v/kT \right], \quad (22)$$

where $v$ is the volume, $T$ the temperature, and $k$ Boltzmann's constant. The prefactor $\nu_{ij}^0$ is given by

$$\nu_{ij}^0 = G \frac{\left| \gamma_0' \right|}{2\pi M_s} \left( c_1^{(i)} c_2^{(i)} \right)^{1/2} \left( c_2^2/c_1 \right)^{1/2}, \quad (23)$$

where $M_s$ is the saturation magnetization, $\alpha$ the damping parameter, $\gamma_0'$ the gyromagnetic factor, and

$$G = \frac{1}{2c_2^2} \left\{ \left( c'_2 - c_1 \right) + \left[ \left( c_1 + c'_2 \right)^2 + 4\alpha^{-2} c_1 c'_2 \right]^{1/2} \right\}. \quad (24)$$

The parameters $c_1^{(i)}$ and $c_2^{(i)}$ are the eigenvalues of the perpendicular Jacobian for the minimum, while $c_1$ and $-c_2$ are those for the saddle point (chosen so $c_1$ and $c_2$ are both positive). These eigenvalues were calculated in Section II B.

For the rest of this article a single-subscript frequency $\nu_i$ refers to a particular combination of initial state and saddle point. These variables are defined in Table I and the parameters needed to calculate them are included. The frequencies are also labelled in Figs. 6-9.

The prefactors, normalized by $2\pi M_s/|\gamma_0 K'_1|$, are displayed in Fig. 4. The normalized prefactor is dimensionless and depends on $\alpha$, $\kappa$, the sign of $K'_1$, and $|K'_1|v/kT$. For the independent variable I use $K_u/|K'_1|$ instead of $\kappa$ because it is easier to interpret. Some of the prefactors diverge to zero or infinity on approaching the three values of $\kappa$ ($-0.2229$, $2/3$ and $0.7611$) at which solutions change stability. In addition, the prefactors for $\nu_3$ ($K'_1 > 0$) and $\nu_5$ ($K'_1 < 0$) have small jumps at $\kappa = 2/3$ associated with the change in connectivity of the $g_{110}$ saddle point (compare Figures 7 and 8). As discussed in N1, these anomalies occur when the assumptions behind the Kramers theory fail. In particular, one or more second derivatives go to zero at a minimum or saddle point (Table I). Higher order expansion may not help because either the minimum or the saddle point is not in local quasiequilibrium. Thus, a numerical solution of the Fokker-Planck equation may be necessary near the critical values of $\kappa$.

The single-barrier rates are plotted in Fig. 5. Because of the strong dependence of each rate on $\exp(-\gamma_0' (g_s - g_i)v/kT)$, the divergences in the prefactors mostly have no visible effect except very close to one of the critical values of $\kappa$. Thus, in practice they are not very important.
TABLE I: Parameters for the relaxation rate over a single barrier. Each rate is defined for a particular combination of energy minimum and saddle point. The parameters are used in (22, 23, 24) to determine the rate. Expressions for the $\lambda^{(j)}$ are given in (21).

<table>
<thead>
<tr>
<th>$\nu$</th>
<th>$v_{\min}$</th>
<th>$v_{\text{saddle}}$</th>
<th>$\lambda_{1}^{(1)}$</th>
<th>$\lambda_{2}^{(1)}$</th>
<th>$\lambda_{+}$</th>
<th>$\lambda_{-}$</th>
<th>$(g_{s} - g_{t})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_{1}$</td>
<td>$g_{100}$</td>
<td>$110_{\perp}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$\lambda_{+}$</td>
<td>$\lambda_{-}$</td>
<td>$K_{u} + K_{c}^{1} / 4 - g_{(1)}^{1}$</td>
</tr>
<tr>
<td>$\nu_{2}$</td>
<td>$u$</td>
<td>$110_{\perp}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$\lambda_{+}$</td>
<td>$\lambda_{-}$</td>
<td>$K_{u} - K_{c}^{1} / 12$</td>
</tr>
<tr>
<td>$\nu_{3}$</td>
<td>$g_{100}$</td>
<td>$g_{110}$</td>
<td>$\lambda_{2}^{(1)}$</td>
<td>$\lambda_{2}^{(1)}$</td>
<td>$\lambda_{+}$</td>
<td>$\lambda_{-}$</td>
<td>$K_{u}^{(2)} - g_{(2)}^{(2)}$</td>
</tr>
<tr>
<td>$\nu_{4}$</td>
<td>$u$</td>
<td>$g_{110}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$2K_{u} - 4K_{c}^{1}$</td>
<td>$\lambda_{+}^{(2)}$</td>
<td>$\lambda_{-}^{(2)}$</td>
<td>$g_{(2)}^{(2)} - K_{c}^{1}$</td>
</tr>
<tr>
<td>$\nu_{5}$</td>
<td>$g_{111}$</td>
<td>$g_{110}$</td>
<td>$\lambda_{3}^{(3)}$</td>
<td>$\lambda_{3}^{(3)}$</td>
<td>$\lambda_{+}^{(3)}$</td>
<td>$\lambda_{-}^{(3)}$</td>
<td>$K_{u} + K_{c}^{1} / 4 - g_{(3)}^{(3)}$</td>
</tr>
<tr>
<td>$\nu_{6}$</td>
<td>$g_{111}$</td>
<td>$110_{\perp}$</td>
<td>$\lambda_{3}^{(3)}$</td>
<td>$\lambda_{3}^{(3)}$</td>
<td>$\lambda_{+}$</td>
<td>$\lambda_{-}$</td>
<td>$K_{u} + K_{c}^{1} / 4 - g_{(3)}^{(3)}$</td>
</tr>
</tbody>
</table>

Values for $\kappa < 2/3$. If $\kappa > 2/3$, the entries for $c_{1}$ and $c_{2}$ should be exchanged.

\[ m_{\perp}(t) = m_{\perp}(0) \exp(-\nu_{\perp}t), \quad (25) \]

The parallel component has up to two relaxation rates and can be written

\[ m_{\parallel}(t) = (m_{\parallel}(0) - A) \exp(-\nu_{\parallel}t) + A \exp(-\nu_{\parallel}'t), \quad (26) \]

If there is only one relaxation rate, $A = 0$ and $\nu_{\parallel}'$ is undefined.

1. $\kappa < -0.2229$

For $\kappa < -0.2229$ there are six $g_{100}$ states, six $110_{\perp}$ states, and two $u$ states (Fig. 6). If $K_{c}^{1} > 0$ the $g_{100}$ states are minima, each connected to two neighbors by $110_{\perp}$ saddle points. Numbering the states in counter-clockwise order about the uniaxial easy axis vector $u$, the transition rate matrix is

\[ \nu_{ij} = \begin{bmatrix} 0 & \nu_{1} & 0 & 0 & 0 \\ \nu_{1} & 0 & \nu_{1} & 0 & 0 \\ 0 & \nu_{1} & 0 & \nu_{1} & 0 \\ 0 & 0 & \nu_{1} & 0 & \nu_{1} \\ \nu_{1} & 0 & 0 & \nu_{1} & 0 \end{bmatrix}, \quad (27) \]

where $\nu_{1}$ is defined in Table I. The relaxation rates for the probability distribution are $4\nu_{1}$, $3\nu_{1}$ (double root), $\nu_{1}$ (double root) and 0 (for the equilibrium distribution). If an ensemble of particles are all initially in state 1, the component $m_{\parallel}$ has a simple exponential decay with initial component $m_{\parallel} = \gamma_{1}^{1}$ and rate $\nu_{\parallel} = 4\nu_{1}$. Thus, in (26), $A = 0$ and $\nu_{\parallel}'$ is undefined. The perpendicular component...
FIG. 6: Equilibrium states and their connections for $\kappa = -0.25$. The u labels a node with moment in the [111] direction. If $K_1^* > 0$ the solid lines are streamlines of the energy gradient connecting saddle points with minima, while the dashed lines connect saddle points with maxima. If $K_1^* < 0$ dashed and solid lines are exchanged, maxima are exchanged with minima and saddle points remain the same. Rates across the energy barriers are indicated with labels and arrows.

has initial value $2|\tilde{\gamma}_1|$ and decays with rate $\nu_1 = \nu_1$. The rates $4\nu_1$ and $\nu_1$ are only two of the three relaxation rates for the probability distribution. The third, $3\nu_3$, has no effect on the moment because its relaxation mode affects both ends of each axis equally.

If $K_1^* < 0$ the minima are the two u states, connected by six 110 states. If all particles are initially in state 1, $m_1 = 1$ and the relaxation rate is $\nu_1 = 12\nu_2$. The rate $\nu_1$ is undefined because the perpendicular component is identically zero.

2. $-0.2229 < \kappa < 2/3$

As $\kappa$ crosses $-0.2229$ the $g_{111}$ and $g_{110}$ states form and move apart. In Fig. 7, for $\kappa = 0.25$, they are well away from each other. For $K_1^* > 0$ each g100 minimum is connected by g110 saddle points to two g100 states in the same hemisphere (that is, same u component). It is also connected by 110 saddle points to two g100 states in the other hemisphere. If the g110 states are numbered in a counterclockwise order about the u direction,

$$
\nu_{ij} = \begin{bmatrix}
0 & \nu_1 & \nu_2 & 0 & \nu_3 & \nu_1 \\
\nu_1 & 0 & \nu_1 & \nu_3 & 0 & \nu_1 \\

\nu_3 & \nu_1 & 0 & \nu_1 & \nu_3 & 0 \\

0 & \nu_3 & 0 & \nu_1 & 0 & \nu_1 \\
\nu_3 & 0 & \nu_3 & 0 & \nu_1 & \nu_3 \\

\nu_1 & \nu_3 & 0 & \nu_3 & \nu_1 & 0
\end{bmatrix}
$$

(28)

If all particles are initially in state 1 then $m_{ij}(0) = |\tilde{\gamma}_1|$, $\nu_{ij} = 4\nu_1$, $\nu_{ij} = 2|\tilde{\gamma}_1|$ and $\nu_{ij} = \nu_1 + 3\nu_3$. Another rate, $3(\nu_1 + \nu_3)$, has no effect on the moment.

If $K_1^* < 0$ there are two $u$ minima and six $g_{111}$ minima. Each $u$ minimum is connected to three $g_{111}$ minima by $g_{110}$ saddle points while each $g_{111}$ minimum is connected to two others by $110_{\perp}$ saddle points. If the states are numbered 1 for one $u$ state, 2–7 for the $g_{111}$ states and 8 for the other $u$ state, with state 2 being connected to state 1,

$$
\nu_{ij} = \begin{bmatrix}
0 & \nu_4 & 0 & \nu_4 & 0 & \nu_4 & 0 & 0 \\
\nu_5 & 0 & \nu_6 & 0 & \nu_6 & 0 & \nu_6 & 0 \\

0 & \nu_6 & 0 & \nu_6 & 0 & \nu_6 & 0 & \nu_5 \\
\nu_5 & 0 & \nu_6 & 0 & \nu_6 & 0 & \nu_6 & 0 \\
0 & \nu_6 & 0 & \nu_6 & 0 & \nu_6 & 0 & \nu_5 \\
0 & \nu_4 & 0 & \nu_4 & 0 & \nu_4 & 0 & \nu_4 \\
0 & \nu_4 & 0 & \nu_4 & 0 & \nu_4 & 0 & \nu_4
\end{bmatrix}
$$

(29)
The nonzero relaxation rates are \( \nu_5 + 3 \nu_4, \nu_5 + 3 \nu_6 \) (double root), \( \nu_5 + \nu_6 \) (double root), and \( \nu_\pm \), where

\[
\nu_\pm = (\beta \pm \sqrt{\alpha})/2, \tag{30}
\]

and

\[
\begin{align*}
\alpha &= (3 \nu_4 - 4 \nu_6)^2 + \nu_5^2 + 6 \nu_5 \nu_4 + 8 \nu_5 \nu_6 \tag{31a} \\
\beta &= \nu_5 + 3 \nu_4 + 4 \nu_6. \tag{31b}
\end{align*}
\]

Of the relaxation rates, only \( \nu_4 \) affect \( m_\parallel \), the component of the moment parallel to the uniaxial axis; and only \( \nu_5 + \nu_6 \) affects the perpendicular component \( m_\perp \). The rates \( \nu_\pm \) do not affect \( m_\perp \) because their relaxation modes (as indicated by the eigenvectors) include probability flow from the \( u \) state equally distributed among the nearest three \( g_{111} \) states. The \( u \) state and the \( g_{111} \) states have a net perpendicular component of zero, so \( m_\perp \) is not affected. Similarly, \( \nu_5 + \nu_6 \) does not affect \( m_\parallel \) because, despite the contribution of \( \nu_5 \), the relaxation mode does not transfer any probability to the \( u \) state.

There are two kinds of state, \( u \) and \( g_{111} \), and \( \dot{m}(t) \) depends on the initial state. For example, suppose all particles are in state 1 (a \( u \) state). From this state there is a probability flow with rate \( \nu_4 \) into the nearest three \( g_{111} \) states (Fig. 7). These states are numbered 2, 4 and 6. The initial rate of change in probability is therefore \( \dot{n}(0) = (-3 \nu_4, \nu_4, 0, 0, 0, 0, 0) \) (the dot indicates a time derivative). Since the parallel components of the \( u \) state and \( g_{111} \) states are 1 and \( |\gamma_3| \), \( \dot{m}_\parallel(0) = 3 \nu_4 |\gamma_3| - 1 \). This is always zero or negative because \( |\gamma_3| \leq 1 \), so \( m_\parallel \) always decreases initially. This is to be expected because all other remanent states have a lower component in the \( u \) direction. The other component, \( m_\perp \), remains zero because of the symmetry.

The derivative of the time dependence of \( m_\parallel \) is very messy, and is left to the electronic supplement. The result is that \( m_\parallel(0) = 1, \nu_\parallel = \nu_-, \nu'_\parallel = \nu_+ \), and

\[
A = \frac{3 \nu_4 - \nu_-}{\sqrt{\alpha}} - \frac{3 \nu_4}{\sqrt{\alpha}} |\gamma_3|. \tag{32}
\]

The first term in \( A \) is the contribution of relaxation between \( u \) states while the second term is that of relaxation between \( g_{111} \) states.

If all particles are in state 2 (a \( g_{111} \) state), \( \dot{n}(0) = (\nu_5, -\nu_5, 2 \nu_6, 0, 0, 0, 0, 0, 0, 0) \). Thus, \( m_\parallel(0) = \nu_5 - |\gamma_3| (\nu_5 + 4 \nu_6) \). Now \( m_\parallel \) can increase or decrease initially, depending on the value of \( |\gamma_3| \). As for the perpendicular component, state 2 has component 2 \( |\beta_3| \), state 1 has component zero, and states 3 and 7 have components \( \pm |\beta_3| \). Thus, \( m_\perp = -2 |\beta_3| (\nu_5 + \nu_6) \).

Solving for the time dependence of the moment, the perpendicular component has initial value \( m_\perp(0) = 2 |\beta_3| \) and relaxation rate \( \nu_\perp = \nu_5 + \nu_6 \), while for the parallel component \( m_\parallel(0) = |\gamma_3|, \nu_\parallel = \nu_-, \nu'_\parallel = \nu_+ \), and

\[
A = -\frac{\nu_5}{\sqrt{\alpha}} + \frac{\nu_- - 3 \nu_4}{\sqrt{\alpha}} |\gamma_3|. \tag{32'}
\]

The perpendicular component is identically zero.

If the initial state is \( g_{100} \), \( m_\parallel(0) = |\gamma_1|, \nu_\parallel = \nu_- \),

\[
A = \frac{3 \nu_4 - \nu_-}{\sqrt{\alpha}} - \frac{3 \nu_4}{\sqrt{\alpha}} |\gamma_1|. \tag{32''}
\]

As \( \kappa \) crosses \( 2/3 \) the \( g_{110} \) states touch the \( u \) direction and then move away again, while the \( u \) state changes stability (Fig. 8). If \( K_1' > 0 \) the \( u \) state is now a minimum and is connected to the nearest \( g_{100} \) states, while those states are only directly connected to \( g_{100} \) states in the other hemisphere. Number the states 1 for the \( u \) state, 2 - 7 for the \( g_{110} \) states (with 2 being connected to the \( u \) state), and 8 for the other \( u \) state. The geometry is then the same as for \( -0.2229 < \kappa < 2/3 \) and \( K_1' < 0 \), with \( g_{111} \) states replaced by \( g_{100} \) states. Thus, \( \nu_5 \) replaced by \( \nu_5, \nu_6 \) by \( \nu_1 \) and \( \gamma_3 \) by \( \gamma_1 \). The frequencies \( \nu_\pm \) are given by (30) with (31) replaced by

\[
\begin{align*}
\alpha &= (3 \nu_4 - 4 \nu_1)^2 + \nu_5^2 + 6 \nu_5 \nu_4 + 8 \nu_5 \nu_1 \tag{31a'} \\
\beta &= \nu_5 + 3 \nu_4 + 4 \nu_1. \tag{31b'}
\end{align*}
\]

If all the moments are initially in the \( u \) direction, \( m_\parallel(0) = 1, \nu_\parallel = \nu_-, \nu'_\parallel = \nu_+ \), and

\[
A = \frac{3 \nu_4 - \nu_-}{\sqrt{\alpha}} - \frac{3 \nu_4}{\sqrt{\alpha}} |\gamma_1|. \tag{32''}
\]

The perpendicular component is identically zero.

If the initial state is \( g_{100} \), \( m_\parallel(0) = |\gamma_1|, \nu_\parallel = \nu_- \),

\[
A = \frac{3 \nu_4 - \nu_-}{\sqrt{\alpha}} - \frac{3 \nu_4}{\sqrt{\alpha}} |\gamma_1|. \tag{32''}
\]
The coefficients for the perpendicular component are

\[ \nu'_{\parallel} = \nu_{\perp}, \quad \text{and} \]

\[ A = \frac{\nu_{3}}{\sqrt{\alpha}} + \frac{\nu_{\perp} - 3\nu_{4}}{\sqrt{\alpha}} |\gamma|, \quad (32') \]

The coefficients for the perpendicular component are

\[ m_{\perp}(0) = 2|\beta| \] and \( \nu_{\perp} = \nu_{1} + \nu_{3}. \)

If \( K_{1}' < 0 \) there are six \( g111 \) minima, each connected to two nearest neighbors by \( 110_{\perp} \) saddle points, and to two next-nearest-neighbors by \( g110 \) saddle points. Thus,

\[ \nu_{ij} = \begin{bmatrix} 0 & \nu_{5} & \nu_{6} & 0 & \nu_{5} & \nu_{6} \\ \nu_{5} & 0 & \nu_{6} & 0 & \nu_{5} & \nu_{6} \\ \nu_{5} & \nu_{6} & 0 & \nu_{5} & 0 & \nu_{5} \\ 0 & \nu_{5} & 0 & \nu_{6} & 0 & \nu_{5} \\ \nu_{6} & 0 & \nu_{5} & 0 & \nu_{6} & 0 \\ \nu_{6} & \nu_{5} & 0 & \nu_{6} & 0 & \nu_{5} \end{bmatrix}. \quad (34) \]

There are three relaxation rates for the probability distribution: \( 4\nu_{6}, \nu_{6} + 3\nu_{5} \) and \( 3(\nu_{5} + \nu_{6}) \). For the moment, \( m_{\parallel}(0) = |\gamma|, \nu_{\parallel} = 4\nu_{6}, m_{\perp}(0) = 2|\beta| \) and \( \nu_{\perp} = \nu_{6} + 3\nu_{5}. \)

4. \( \kappa > 0.7611 \)

As \( \kappa \) crosses 0.7611 the \( g110 \) and \( g100 \) states meet and annihilate each other. This leaves the \( u, g111 \) and \( 110_{\perp} \) states. If \( K_{1}' > 0 \) the minima are the two \( u \) states, connected to each other by six \( 110_{\perp} \) saddle points (Fig. 9). Thus, \( m_{\parallel}(0) = 1, \nu_{\parallel} = 12\nu_{2} \) and the perpendicular component is zero.

If \( K_{1}' < 0 \) there are six \( g111 \) minima, each connected to two nearest neighbors across \( 110_{\perp} \) saddle points. The geometry is the same as for \( \kappa < -0.2229 \) and \( K_{1}' > 0 \), so \( m_{\parallel}(0) = |\gamma|, \nu_{\parallel} = 4\nu_{6}, m_{\perp}(0) = 2|\beta| \) and \( \nu_{\perp} = \nu_{6}. \)

III. DISCUSSION

The time evolution of the magnetization is given by (25) for the perpendicular component and (26) for the parallel component. The parameters for these equations, including the initial values of the moment, relaxation rates, and prefactor \( A \), are summarized in Table II. I have also provided a MATLAB® function in the electronic supplement to calculate them.

The relaxation rates and prefactor \( A \) are plotted in Fig. 10 for iron (an example of \( K_{1}' > 0 \)). When \( K_{u} < 0 \) the changes in moment are dominated by flow between \( g100 \) states across \( 110_{\perp} \) barriers (rate \( \nu_{1} \)). This determines both the parallel and perpendicular components, so \( \nu_{\parallel} = \nu_{\perp}. \) Once \( K_{u} \) is positive, flow across \( g110 \) barriers (rate \( \nu_{3} \)) becomes faster. This dominates the perpendicular component, but does not affect the parallel component, so the latter is still determined by the slower rate \( \nu_{1}. \) As \( K_{u} \) increases \( \nu_{1} \) decreases and \( \nu_{\perp} \) increases.

For \( K_{u} \) between 2/3 and 0.7611 there are two kinds of states, \( u \) and \( g100 \). There are now two relaxation rates for \( m_{\parallel} \), but still only one for \( m_{\perp} \) (as discussed in section II D 2 for \( K_{1}' < 0 \)). An example of the time dependence of \( m_{\parallel} \) for this case is shown in Fig. 11. The relaxation occurs in two stages. First, a local equilibrium is established between the \( u \) state and the three \( g100 \) states in the same hemisphere. By local equilibrium I mean that
TABLE II: Parameters that determine the time dependence of the magnetization in (25-26).

<table>
<thead>
<tr>
<th>$K_u/K'_u$</th>
<th>Initial state</th>
<th>$m_\parallel(0)$</th>
<th>$A/\langle A \rangle$</th>
<th>$\nu_\parallel$</th>
<th>$\nu'_\parallel$</th>
<th>$m_\perp(0)$</th>
<th>$\nu_\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>($-\infty, -0.2229$)</td>
<td>g100</td>
<td>$\gamma_1$</td>
<td>0</td>
<td>$4\nu_1$</td>
<td>$-2</td>
<td>\beta_1</td>
</tr>
<tr>
<td>1</td>
<td>($-0.2229, 2/3$)</td>
<td>g100</td>
<td>$\gamma_1$</td>
<td>0</td>
<td>$4\nu_1$</td>
<td>$-2</td>
<td>\beta_1</td>
</tr>
<tr>
<td>1</td>
<td>($2/3, 0.7611$)</td>
<td>g100</td>
<td>$\gamma_1$</td>
<td>$-\nu_3 + (\nu_+ - 3\nu_4)</td>
<td>\gamma_1</td>
<td>^3$</td>
<td>$\nu_{-4}^a$</td>
</tr>
<tr>
<td>1</td>
<td>($2/3, 0.7611$)</td>
<td>u</td>
<td>1</td>
<td>$3\nu_4 - \nu_+ - 3\nu_4</td>
<td>\gamma_1</td>
<td>^3$</td>
<td>$\nu_{-4}^b$</td>
</tr>
<tr>
<td>1</td>
<td>($0.7611, \infty$)</td>
<td>u</td>
<td>1</td>
<td>0</td>
<td>$12\nu_2$</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*where $\nu_\perp$ are given by (30) and $\alpha, \beta$ by (31)*

*where $\nu_\perp$ are given by (30) and $\alpha, \beta$ by (31)*

the detailed balance condition is satisfied between these four states. This leads to a decrease in $m_\parallel$ when the initial state is the u state and an increase when the initial state is g100 (the latter being reflected in the small negative value of $A$). This process occurs over a time scale $\left(\nu'_\parallel\right)^{-1}$. Since the quasi-equilibrium distribution is the same for both initial states, the moment is subsequently independent of the initial state. There is then a flow from one hemisphere to the other over the much longer time scale of $\left(\nu_\parallel\right)^{-1}$.

For $K_u > 0.7611K'_u$ the only remnant states are $u$ states. There is then no perpendicular component and the parallel component is governed by a straightforward uniaxial-type relaxation with rate $12\nu_2$.

The relaxation rates and prefactor $A$ are plotted in Fig. 12 for nickel ($K'_u < 0$). The g111 state is the only stable state for $K_u < -2/3|K'_u|$, the u state is the only stable state for $K_u > 0.2229|K'_u|$, and in between the states coexist. Thus, the overlap is much greater than for $K'_u > 0$. The rate $\nu_\parallel$ is always defined but $\nu_\perp$ is only defined where the g111 state is stable. In the overlap region there are two relaxation rates for $m_\parallel$. As for $K'_u > 0$, rates $\nu_\parallel$ and $\nu_\perp$ are nearly equal when $K_u < 0$ and diverge when $K_u > 0$. Where they diverge, $\nu'_\parallel \approx \nu_\perp$.

When $K_u < 0$, $\nu_\parallel$ (the rate for crossing g110 barriers from g111 states) is much smaller than the other two single-barrier rates, $\nu_4$ and $\nu_6$. This, with the equations for $\nu_\parallel$ and $\nu'_\parallel$, implies that $\nu'_\parallel \approx \max(3\nu_4, 4\nu_6)$ and $\nu_\parallel \approx \min(3\nu_4, 4\nu_6)$. Over a very narrow interval between $K_u = -2/3|K'_u|$ and the point where $3\nu_4 = 4\nu_6$, the curves appear to cross. In reality, they bend sharply away from each other. To see this, one would need to magnify the plot by orders of magnitude.

The single-state regions are straightforward, so I will focus on the overlap region. For $-2/3|K'_u| < K_u < 0.2229|K'_u|$, the shape of the curve $m_\parallel(t)$ depends on whether the initial state is $u$ or g111. The relationship between the curves depends on the energies of the states and the relaxation rates $\nu_\parallel$ and $\nu'_\parallel$. Three examples are shown in Fig. 13.

For $K_u < 0$, the g111 states have lower energy than the u states, so the probability flows towards the g111 states. Thus, the moment decreases more quickly if the initial state is $u$. For $K_u = -0.64|K'_u|$, there are sharp swings in $A$, but this has little effect because $\nu'_\parallel \approx \nu_\parallel$.

FIG. 11: Time evolution of the parallel component of the moment. Solid line: initial state is $u$. Dashed line: initial state is $g100$.

FIG. 12: (a) Relaxation rates for nickel (same parameters as in Fig. 5b). (b) Parameter $A$ in the prefactor for rates $\nu_\parallel$, $\nu'_\parallel$. As depicted, some rates are only defined for a particular starting state.
creasing slowly as the magnitude as $K_u$ decreases. All perpendicular components have a critical separation of the rates. On the time scale ($\tau$) becomes saturated in the theory establishment. The magnetization for local equilibrium to be established. The magnetization for $K'_u < 0$ and $K_u > 0$, the moment increases to saturation at the rate $\nu'_u$ before decreasing at the rate $\nu_u$.

The initial values and relaxation rates listed in Table II have been derived for samples in which all the particles are oriented the same way and start out in the same state. If there is more than one initial state, the magnetic moment is the sum of the moment vectors for each state. If the orientations vary, the moment must be integrated over the distribution of orientations. This is fairly straightforward if there is only one type of remanent state (for example, $g111$) because then all particles still have the same relaxation rates $\nu_u$ and $\nu'_u$. Only the initial value of the moment changes. It is more complicated if there are two types of remanent state because they have different time dependence, at least until a local equilibrium is established. The initial distribution between the two kinds of state can also be difficult to calculate for a given magnetic experiment.

The theory developed in this article and in N1 has the most striking consequences for samples with oriented particles. If $K_u > 0$ and all the uniaxial easy axes are aligned, there can be a strong anisotropy in the relaxation rate, with relaxation being much faster if the particles are magnetized perpendicular to the easy axes than if they are magnetized parallel. Indeed, in the latter case the magnetization can even increase to saturation before decreasing. These changes also imply a rotation of the moment towards the easy axis.

**IV. CONCLUSIONS**

In two articles I have calculated superparamagnetic relaxation times for combined cubic and uniaxial anisotropy. In part I the uniaxial axis is in a (001) direction while in this part it is in a (111) direction. The new theory departs from the Néel-Brown theory in some striking ways. Instead of one relaxation rate for the distribution of probability between states, there are up to five. However, some relaxation modes do not affect the magnetic moment. Those that do are anisotropic, so that components parallel to the uniaxial easy axis and perpendicular to it have different relaxation rates. When the uniaxial anisotropy is prolate ($K_u > 0$) the parallel rate decreases as $K_u$ increases while the perpendicular rate increases. At a critical value of $K_u/|K'_u|$, the perpendicular component disappears.

The (111) orientation also differs from the (001) orientation in significant respects. When the uniaxial anisotropy is oblate ($K_u < 0$), the rates for parallel and perpendicular components remain close together instead of diverging. Also, the parallel component can have two relaxation rates. When $K'_u > 0$ and $0 < K_u < 0.2229|K'_u|$
the faster relaxation mode saturates the parallel component instead of decreasing it.

The multiple relaxation modes have some important implications. A single particle can have more than one superparamagnetic/single-domain critical size and more than one blocking temperature. Between critical sizes, a local equilibrium is established between some of the remanent states. This reduces the remanence. Finally, if a sample has oriented particles, the relaxation rate depends on direction, and at the faster rate the magnetic moment will rotate. The latter predictions can also be expected to apply to particles above the single-domain size range.

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