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Master Equation in Phase Space for a Spin in an Arbitrarily Directed Uniform External Field

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Abstract The time evolution equation for the probability density function of spin orientations in the phase space representation of the polar and azimuthal angles is derived for the nonaxially symmetric problem of a quantum paramagnet subjected to a uniform magnetic field of *arbitrary* direction. This is accomplished by first rotating the coordinate system into one in which the polar axis is collinear with the field vector, then writing the reduced density matrix equation in the new coordinate system as an explicit inverse Wigner-Stratonovich transformation so that the phase space master equation may be derived just as in the axially symmetric case [Yu.P. Kalmykov et al., J. Stat. Phys. 131:969, 2008]. The properties of this equation, resembling the corresponding Fokker-Planck equation, are investigated. In particular, in the large spin limit, $S \to \infty$, the master equation becomes the classical Fokker-Planck equation describing the magnetization dynamics of a classical paramagnet in an *arbitrarily* directed uniform external field.

Keywords Spins · Quasi-probability distributions · Wigner distributions · Master equation · Fokker-Planck equation

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1 Introduction

Phase space representations of quantum mechanical evolution equations provide a formal means of treating quantum effects in dynamical systems linking transparently to the classical representations, thereby allowing one to calculate quantum corrections to classical distribution functions [1, 2]. Such representations which are generally based on the coherent state representation of the density matrix introduced by Glauber and Sudarshan and widespread in quantum optics [2, 3] may also be applied to spin systems (e.g., [4–17]). They then allow one to analyse quantum spin relaxation using a master equation for a *quasi-probability distribution function* $W(\vartheta, \varphi, t)$ of spin orientations in a phase (here configuration) space (ϑ, φ); ϑ and φ are the classically meaningful polar and azimuthal angles. Thus mapping of the quantum spin dynamics onto c-number quasi-probability density evolution equations clearly shows how these equations reduce to the Fokker-Planck equation in the classical limit [7–9, 15–17]. The phase space distribution function for spins having been introduced by Stratonovich [18] for closed systems, was extensively developed both for closed and open spin systems [4, 5, 7–28]. It is entirely analogous to the translational Wigner distribution $W(x, p, t)$ in the phase space of positions and momenta (x, p) [29], which is a certain Fourier transform corresponding to a quasi-probability representation of the density matrix operator $\hat{\rho}(t)$. However, particular differences arise because of the angular momentum commutation relations, e.g., the Wigner function takes the form of a finite linear combination of the spherical harmonics. Nevertheless the phase space distribution (Wigner) function $W(\vartheta, \varphi, t)$ of spin orientations in a configuration space, just as the Wigner function $W(x, p, t)$ for the translational motion of a particle, enables the expected value $\langle \hat{A} \rangle(t)$ of a quantum spin operator $\hat{A}$ to be calculated via the corresponding c-number (or Weyl symbol) function $A(\vartheta, \varphi)$. Thus quantum mechanical averages involving the spin density matrix may be calculated just as classical ones which is naturally suited to the calculation of quantum corrections [2]. Moreover, the formalism is easy to implement because the diffusion-like equation form of the master equations governing the time evolution of phase space distributions enables powerful computational techniques originally developed for the solution of classical Fokker-Planck equations for the rotational Brownian motion of classical magnetic dipoles (e.g., continued fractions, mean first passage times, etc. [30, 31]) to be seamlessly carried over into the quantum domain [15–17, 32–39].

We stress that both the phase space and density matrix representations, although having outwardly different forms, are entirely equivalent [17, 40, 41]. Now several other quantum, semiclassical, and classical methods for the description of spin dynamics already exist besides the phase space (generalized coherent state) [4–14] treatment, e.g., the reduced density matrix [42, 43], the stochastic Liouville equation [4, 5, 44], the Langevin equation [30]. In general, however, phase space methods map quantum mechanical evolution equations for the (reduced) density matrix for spins onto a c-number space. Thus they have an obvious advantage over the operator equations in studying the quantum/classical divide since the phase space representation of the density operator, is rendered in powers of the inverse spin value S^{-1}. Nevertheless, phase space methods for spins have hitherto been almost exclusively used in quantum optics and very little attention has been paid to other spin systems. For example, the explicit master equation for the phase space distribution function $W(\vartheta, \varphi, t)$ for the axially symmetric problem of a paramagnet of arbitrary S in an external *constant* uniform magnetic field $\mathbf{H}$ applied along the Z axis (i.e., the Hamiltonian $\beta \hat{H}_S = -\xi \hat{S}_Z$) has been virtually the only spin system considered until recently [4, 5, 7, 8, 10–15] with the sole exception of Refs. [16, 17], where uniaxial anisotropy was also included, so that $\beta \hat{H}_S = -\xi \hat{S}_Z - \sigma \hat{S}_Z^2$ and so the problem remains axially symmetric. Thus the diagonal terms of the density matrix always decouple from the non-diagonal ones and only the former partake in the time evolution which is not so for nonaxially symmetric problems [16, 17]. Here $\hat{S}_Z$ is the Z-component of the spin operator $\hat{\mathbf{S}}$, $\xi = \beta\hbar\omega_0$, $\omega_0 = \gamma H$ is the precession (Larmor) frequency, γ is the gyromagnetic ratio, σ is the anisotropy constant, $\beta = 1/(kT)$ is the inverse thermal energy, and $\hbar$ is Planck's reduced constant.

We emphasize that in order to determine the relevant phase space master equation (by the Wigner-Stratonovich transformation as detailed in [16]), one must first determine the evolution equation for the *reduced* spin density matrix for each *particular* spin Hamiltonian unlike the situation for point particles where a canonical form of that equation exists *regardless* of the form of the Hamiltonian. Now in order to write the evolution equation, one must determine the collision kernel matrix representing the interaction between the spin and bath. This gives rise to considerable difficulties in the evaluation of the commutators of spin operators and the density matrix and the corresponding phase space representations for *nonaxially* symmetric Hamiltonians, where nondiagonal elements of the density matrix now partake in the time evolution, which are the most interesting cases. Hence a new approach using a coordinate system, in which the density matrix can be diagonalized, is necessary. In order to illustrate this, we shall treat the simplest possible nonaxially symmetric problem. Thus we shall study the nonaxially symmetric, *time-independent*, Hamiltonian $\hat{H}_S$, corresponding to a single spin in a uniform external field $\mathbf{H}$ with an *arbitrary* direction in space, so that

$$\beta\hat{H}_S = -\beta\gamma\hbar\hat{\mathbf{S}}\cdot\mathbf{H} = -\xi_X\hat{S}_X - \xi_Y\hat{S}_Y - \xi_Z\hat{S}_Z, \tag{1}$$

where ξ_X, ξ_Y, ξ_Z and $\hat{S}_X$, $\hat{S}_Y$, $\hat{S}_Z$ are, respectively, the Cartesian components of the dimensionless magnetic field vector $\boldsymbol{\xi} = \beta\gamma\hbar\mathbf{H}$ and the spin operator $\hat{\mathbf{S}}$.

2 Evolution Equation for the Reduced Density Matrix

We write the total Hamiltonian corresponding to a spin interacting with a heat bath as [4, 5, 7, 44]

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B, \tag{2}$$

where $\hat{H}_S$, $\hat{H}_{SB}$, $\hat{H}_B$ are the Hamiltonians of the spin, the spin-bath interaction, and the bath respectively. The spin-bath interaction Hamiltonian $\hat{H}_{SB}$ is [7, 16, 45]

$$\hat{H}_{SB} = -\hbar\gamma\hat{\mathbf{S}}\cdot\hat{\mathbf{h}}^{\dagger}, \tag{3}$$

where $\hat{\mathbf{h}}$ is the random noise field operator characterizing the collision damping (due to the bath) incurred by the precessional motion of the spin and is essentially the bath variable, and the symbol † denotes the Hermitian conjugate. It is unnecessary to write explicitly the bath Hamiltonian, since we are only interested in the dynamics of the spin.

Now the evolution equation for the reduced density matrix $\hat{\rho}$ is given by the quantum Liouville equation from which the bath degrees of freedom can be projected out. Hence we have the Nakajima-Zwanzig equation concerning the spin [16], from which two commonly used approximations stem, namely that the spin-bath coupling gives rise to a Markov process and that we have weak spin-bath interactions. Under these assumptions, the reduced master equation for an arbitrary Hamiltonian is [4, 5, 7, 16, 44]

$$\frac{\partial\hat{\rho}(t)}{\partial t} + \frac{i}{\hbar}\big[\hat{H}_S, \hat{\rho}(t)\big] = \mathrm{St}\{\hat{\rho}(t)\}, \tag{4}$$

where the collision kernel matrix $\mathrm{St}\{\hat{\rho}(t)\}$ characterizing the spin-bath interaction is given by

$$\mathrm{St}\{\hat{\rho}(t)\} = -(\hbar^2 Z_B)^{-1} \int_0^\infty d\tau \,\mathrm{Tr}_B\big\{\big[\hat{H}_{SB}, e^{-i(\hat{H}_S+\hat{H}_B)\tau/\hbar}\big[\hat{H}_{SB}, \hat{\rho}_B^{eq}\hat{\rho}(t)\big]e^{i(\hat{H}_S+\hat{H}_B)\tau/\hbar}\big]\big\}. \tag{5}$$

Here $\hat{\rho}_B^{eq}$ is the equilibrium density matrix of the bath which in general is nondiagonal unlike the axially symmetric case and Z_B is the corresponding partition function. Equation (4) describes the evolution of the reduced density matrix of spins in contact with the thermal bath. The collision kernel in the form of (5), with the spin-bath interaction Hamiltonian explicitly given by (3), is selected because it represents the direct quantum analogue of the Fokker-Planck equation for the rotational diffusion of a classical spin since we are now dealing with white noise operators.

We now specialize to a spin in an arbitrarily directed uniform field. We can then rewrite the spin Hamiltonian (1) as

$$\beta\hat{H}_S = -\xi\hat{\mathbf{S}}\cdot\mathbf{u}_H^\dagger = -\xi\sum_{\mu=-1}^{1} u_H^\mu \hat{S}_\mu, \tag{6}$$

where $\hat{S}_0 = \hat{S}_Z$, $\hat{S}_{\pm1} = \mp(\hat{S}_X \pm i\hat{S}_Y)/\sqrt{2}$ and $u_H^0 = \xi_Z/\xi$, $u_H^{\pm1} = \mp(\xi_X \mp i\xi_Y)/(\sqrt{2}\xi)$ are, respectively, the *spherical components* of the spin operator $\hat{\mathbf{S}}$ and the unit vector $\mathbf{u}_H^\dagger = (u_H^{+1}, u_H^0, u_H^{-1})^T$ along the arbitrarily directed magnetic field $\mathbf{H}$, upper and lower indices denote contravariant and covariant components, correspondingly [46], and the transpose symbol T is mapping a row-vector to a column-vector. The spherical components of $\mathbf{u}_H^\dagger$ can in turn be expressed in terms of the polar and azimuthal angles ϑ_H and φ_H (the source coordinates) specifying the orientation of the uniform magnetic field $\mathbf{H}$ in spherical polar coordinates

$$u_H^0 = \cos\vartheta_H, \qquad u_H^{\pm1} = \mp\sin\vartheta_H e^{\mp i\varphi_H}/\sqrt{2}, \tag{7}$$

where $\vartheta_H = \arccos\xi_Z/\xi$ and $\varphi_H = \arctan\xi_Y/\xi_X$. We can now reduce the problem to one in which only the diagonal elements of the density matrix participate in the time evolution by introducing a new coordinate system $X'Y'Z'$ with the new polar axis Z' directed along the uniform magnetic field axis $\mathbf{H}$ instead of the field being in an arbitrary direction. In the coordinate system $X'Y'Z'$, the transformed spherical components $\hat{S}'_\mu$ of $\hat{\mathbf{S}}'$ may be related to those of the operator $\hat{\mathbf{S}}$ as [46]

$$\hat{\mathbf{S}}' = \hat{\mathbf{S}}\mathbf{A} \quad \text{or} \quad \hat{S}'_\mu = \sum_{\mu'=-1}^{1} A_{\mu',\mu}\hat{S}_{\mu'}, \tag{8}$$

where the matrix elements $A_{\mu',\mu}$ of the transformation matrix $\mathbf{A}$ are defined as

$$A_{\mu',\mu} = D^1_{\mu',\mu}(\varphi_H, \vartheta_H, 0), \tag{9}$$

$D^L_{M,M'}(\alpha,\beta,\gamma)$ is the Wigner D function, and α,β,γ are the Euler angles [46]. In order to obtain the transformation given by (8), we have used the property of the *polarization operators*, $\hat{T}^{(S)}_{L,M}$, that on transformation of the coordinate system, under rotations specified by the Euler angles α,β,γ, the polarization operators transform as [46]

$$\hat{T}'^{(S)}_{L,M'} = \sum_M D^L_{M,M'}(\alpha,\beta,\gamma)\hat{T}^{(S)}_{L,M}, \tag{10}$$

where we have recalled that the spherical components of the spin operator can be represented in terms of the $\hat{T}^{(S)}_{L,M}$ as [46]

$$\hat{S}_\mu = \sqrt{S(S+1)(2S+1)/3}\,\hat{T}^{(S)}_{1,\mu}. \tag{11}$$

Thus the spin Hamiltonian (6) can be written in the new coordinate system as

$$\beta \hat{H}'_S = -\xi \hat{S}'_0, \tag{12}$$

which is of the *same form* as the Hamiltonian for the axially symmetric problem of a uniform field applied along the polar axis as treated in [16] (with zero anisotropy).

Having transformed the Hamiltonian to the axially symmetric form given by (12), the master equation (4) in the rotated coordinate system becomes (see Appendix A)

$$\begin{aligned}\frac{\partial \hat{\rho}'(t)}{\partial t} - \frac{i\xi}{\hbar\beta}\big[\hat{S}'_0, \hat{\rho}'(t)\big] &= D_\parallel\big(\big[\hat{S}'_0\hat{\rho}'(t), \hat{S}'_0\big] + \big[\hat{S}'_0, \hat{\rho}'(t)\hat{S}'_0\big]\big)\\ &\quad + D_\perp\big(e^\xi\big[\hat{S}'_{+1}\hat{\rho}'(t), \hat{S}'_{-1}\big] + e^\xi\big[\hat{S}'_{+1}, \hat{\rho}'(t)\hat{S}'_{-1}\big]\\ &\quad + \big[\hat{S}'_{-1}\hat{\rho}'(t), \hat{S}'_{+1}\big] + \big[\hat{S}'_{-1}, \hat{\rho}'(t)\hat{S}'_{+1}\big]\big),\end{aligned} \tag{13}$$

where $D_\parallel$ and $D_\perp$ are effective diffusion coefficients defined in Appendix A. This equation is of exactly the *same form* [15, 16] as the reduced density matrix evolution equation for the *axially symmetric* Hamiltonian $\beta\hat{H}_S = -\xi\hat{S}_Z$, where only the diagonal terms contribute to the time evolution. We note that the commutators $[\hat{S}'_0, \hat{\rho}'(t)\hat{S}'_0]$, $[\hat{S}'_{+1}, \hat{\rho}'(t)\hat{S}'_{-1}]$, and $[\hat{S}'_{-1}, \hat{\rho}'(t)\hat{S}'_{+1}]$ in (13) are, respectively, the complex conjugates of $[\hat{S}'_0\hat{\rho}'(t), \hat{S}'_0]$, $[\hat{S}'_{+1}\hat{\rho}'(t), \hat{S}'_{-1}]$, and $[\hat{S}'_{-1}\hat{\rho}'(t), \hat{S}'_{+1}]$. The collision kernel in (13) can also be rewritten in compact vector form as

$$\mathrm{St}\{\hat{\rho}'(t)\} = 2\hat{\mathbf{S}}'\hat{\rho}'(t)\mathbf{E}^\xi_+\mathbf{D}\hat{\mathbf{S}}'^\dagger - \hat{\mathbf{S}}'\mathbf{E}^\xi_-\mathbf{D}\hat{\mathbf{S}}'^\dagger\hat{\rho}'(t) - \hat{\rho}'(t)\hat{\mathbf{S}}'\mathbf{E}^\xi_-\mathbf{D}\hat{\mathbf{S}}'^\dagger. \tag{14}$$

Here $\mathbf{D}$ represents a diffusion tensor with elements

$$[\mathbf{D}]_{\mu'\mu} = \delta_{\mu'\mu}[D_\parallel\delta_{\mu,0} + D_\perp(1-\delta_{\mu,0})] \tag{15}$$

and the matrices $\mathbf{E}^\xi_+$ and $\mathbf{E}^\xi_-$ are

$$\mathbf{E}^\xi_\pm = \begin{pmatrix} -e^\xi\delta_{1,\pm1} - \delta_{1,\mp1} & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & -e^\xi\delta_{1,\mp1} - \delta_{1,\pm1}\end{pmatrix}. \tag{16}$$

Using the transformation given by (8), the collision term in (13) may be written in the original coordinate system XYZ, as

$$\begin{aligned}\mathrm{St}\{\hat{\rho}(t)\} &= D_\parallel\sum_{\mu',\mu''=-1}^{1} D^1_{\mu',0}(\varphi_H,\vartheta_H,0)D^1_{\mu'',0}(\varphi_H,\vartheta_H,0)\big(\big[\hat{S}_{\mu'}\hat{\rho}(t), \hat{S}_{\mu''}\big] + \big[\hat{S}_{\mu'}, \hat{\rho}(t)\hat{S}_{\mu''}\big]\big)\\ &\quad + D_\perp e^\xi\sum_{\mu',\mu''=-1}^{1} D^1_{\mu',+1}(\varphi_H,\vartheta_H,0)D^1_{\mu'',-1}(\varphi_H,\vartheta_H,0)\\ &\quad \times\big(\big[\hat{S}_{\mu'}\hat{\rho}(t), \hat{S}_{\mu''}\big] + \big[\hat{S}_{\mu'}, \hat{\rho}(t)\hat{S}_{\mu''}\big]\big)\end{aligned}$$

$$+ D_\perp \sum_{\mu',\mu''=-1}^{1} D^1_{\mu',-1}(\varphi_H, \vartheta_H, 0) D^1_{\mu'',+1}(\varphi_H, \vartheta_H, 0)$$
$$\times \left(\left[\hat{S}_{\mu'} \hat{\rho}(t), \hat{S}_{\mu''}\right] + \left[\hat{S}_{\mu'}, \hat{\rho}(t) \hat{S}_{\mu''}\right]\right) \tag{17}$$

or alternatively in the vector form (cf. (9)).

$$\mathrm{St}\{\hat{\rho}(t)\} = 2\hat{\mathbf{S}}\mathbf{A}\hat{\rho}(t)\mathbf{E}^{\xi}_{+}\mathbf{D}(\hat{\mathbf{S}}\mathbf{A})^{\dagger} - \hat{\mathbf{S}}\mathbf{A}\mathbf{E}^{\xi}_{-}\mathbf{D}(\hat{\mathbf{S}}\mathbf{A})^{\dagger}\hat{\rho}(t) - \hat{\rho}(t)\hat{\mathbf{S}}\mathbf{A}\mathbf{E}^{\xi}_{-}(\hat{\mathbf{S}}\mathbf{A})^{\dagger}. \tag{18}$$

The collision kernel defined by (17) is rendered zero by the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta \hat{H}_S}/Z_S$, where $Z_S = \mathrm{Tr}\{e^{-\beta \hat{H}_S}\}$ is the partition function. This is most easily seen in the new coordinate system, simply by direct substitution of the equilibrium spin density matrix $\hat{\rho}'_{eq} = e^{\xi \hat{S}'_0}/Z_S$ into the new master equation (13) and then using the operator equality

$$e^{\xi \hat{S}'_0} \hat{S}'_{\pm 1} e^{-\xi \hat{S}'_0} = e^{\pm \xi} \hat{S}'_{\pm 1} \tag{19}$$

to simplify the various commutators. Thus we have shown how the reduced density matrix equation for the *nonaxially symmetric* problem of an *arbitrarily directed* uniform field may be treated via a simple rotation of the coordinate system using the methods previously developed [13, 15] for the *axially symmetric* problem of a uniform field applied along the Z axis.

The conditions for the validity of the reduced density matrix evolution so obtained have been discussed in detail in Refs. [7, 10, 16] and may be briefly summarized as follows. Essentially, that equation follows from the equation of motion of the reduced density matrix in the rotating-wave approximation (familiar in quantum optics, where counter-rotating, rapidly oscillating terms are averaged out) and applies in the narrowing limit case when the correlation time τ_c of the random field acting on the spin satisfies the condition $\gamma H \tau_c \ll 1$, where H is the averaged amplitude of the random magnetic field. Thus we implicitly imply that the interactions between the spin and the heat bath are small enough to ensure the validity of the weak coupling limit and that the correlation time characterizing the bath is so short that the stochastic process originating in the bath is Markovian [5, 33]. Hence one may assume Ohmic damping. These approximations may be used in the high temperature limit, $\beta|\varepsilon_m - \varepsilon_{m\pm 1}| \ll 1$, where ε_m, $\varepsilon_{m\pm 1}$ are the energy eigenvalues. In the parameter range, where the approximation fails (e.g., throughout the very low temperature region), more general forms of the phase space and density matrix equations must be used (such as treated, e.g., in Refs. [47–49]). Nevertheless, we still use the model based on the above approximation because despite many drawbacks it can qualitatively describe the relaxation in spin systems. Moreover, the model can be regarded as the direct quantum generalization of the Langevin formalism used by Brown in his theory of relaxation of classical spins [50, 51].

Having obtained the evolution equation (for the reduced density matrix) for this simple nonaxially symmetric problem we shall now illustrate how the corresponding master equation in phase space can be obtained using the properties of the Wigner-Stratonovich transformation and its inverse.

3 Wigner-Stratonovich Transformation of the Density Matrix Evolution Equation

First recall that phase space representations of quantum mechanical evolution equations when applied to spin systems characterized by a Hamiltonian $\hat{H}_S$, allow one to analyse the spin relaxation using a master equation for a *quasi-probability* function $W_S^{(s)}(\vartheta, \varphi, t)$ of spin orientations in a phase (here configuration) space (ϑ, φ) which is classically meaningful. Here ϑ and φ are the polar and azimuthal angles, S is as before the spin size and the parameter (s) characterizes various quasi-probability functions of spins belonging to the $SU(2)$ dynamical symmetry group. The parameter values $s = 0$ and $s = \pm 1$ correspond to the Berezin [19] and Stratonovich [18] contravariant and covariant functions, respectively (the latter are directly related to the P and Q symbols appearing naturally in the coherent state representation [2, 52]). We therefore seek an evolution equation for the Wigner distribution function $W_S^{(s)}(\vartheta, \varphi, t)$, i.e., we desire an equation of the form

$$\frac{\partial W_S^{(s)}}{\partial t} = L_S W_S^{(s)}, \tag{20}$$

where L_S is a linear differential operator depending on $\hat{H}_S$. This equation will now be explicitly derived for our nonaxially symmetric problem by mapping onto phase space the evolution equation (4) for the reduced density matrix with collision operator given by (17). The first step is to simplify the various commutators using the properties of the polarization operators and spherical harmonics so that the terms involving them appear as inverse Wigner-Stratonovich transformations [cf. (22) below] of differential operators acting on the phase space distribution. (Speaking in a universal sense, the problem is to transform reduced density matrix evolution equations of the generic form of (4) into the phase space representation.) The transformation to phase space may then be explicitly accomplished because $W_S^{(s)}(\vartheta, \varphi, t)$ and $\hat{\rho}$ are related via the bijective map [52]

$$W_S^{(s)}(\vartheta, \varphi, t) = \mathrm{Tr}\{\hat{\rho}(t)\hat{w}_s(\vartheta, \varphi)\}, \tag{21}$$

$$\hat{\rho}(t) = \frac{2S+1}{4\pi} \int \hat{w}_s(\vartheta, \varphi) W_S^{(-s)}(\vartheta, \varphi, t) d\Omega, \tag{22}$$

where the Wigner-Stratonovich operator (or kernel of the transformation) $\hat{w}_s(\vartheta, \varphi)$ is defined as the finite linear combination of polarization operators

$$\hat{w}_s(\vartheta, \varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} (C_{S,S,L,0}^{S,S})^{-s} Y_{L,M}^{*}(\vartheta, \varphi) \hat{T}_{L,M}^{(S)}. \tag{23}$$

Here $\mathrm{Tr}\{\hat{w}_s\} = 1$ and $[(2S+1)/4\pi] \int \hat{w}_s d\Omega = \hat{I}^{(S)}$ ($\hat{I}^{(S)}$ is the identity matrix), the asterisk denotes the complex conjugate, $Y_{L,M}(\vartheta, \varphi)$ are the spherical harmonics [46], $\hat{T}_{L,M}^{(S)}$ are the polarization operators [46], $C_{S,S,L,0}^{S,S}$ are the Clebsch-Gordan coefficients [46], and $d\Omega = \sin\vartheta\, d\vartheta\, d\varphi$. Either the density matrix $\hat{\rho}$ or the phase space representation $W_S^{(s)}(\vartheta, \varphi, t)$ allow one to calculate the *average* value of an arbitrary spin operator $\hat{A}$ as

$$\langle \hat{A} \rangle = \mathrm{Tr}\{\hat{\rho}\hat{A}\}$$

or

$$\langle \hat{A} \rangle = \frac{2S+1}{4\pi} \int A^{(s)}(\vartheta, \varphi) W_S^{(-s)}(\vartheta, \varphi, t) d\Omega,$$

respectively, where $A^{(s)}(\vartheta, \varphi) = \mathrm{Tr}\{\hat{A}\hat{w}_s(\vartheta, \varphi)\}$ is the Weyl symbol of $\hat{A}$. We consider below only $W_S^{(-1)}$ [omitting everywhere the superscript -1 in $W_S^{(-1)}$, i.e., $W_S^{(-1)} \to W_S$] because

[52] it alone satisfies the non-negativity condition required of a true probability density function, viz., $W^{(-1)} \geq 0$. We remark in passing that the phase-space distribution W_S may be presented for arbitrary S in terms of a finite linear combination of the spherical harmonics [52], namely,

$$W_S(\vartheta, \varphi, t) = \frac{4\pi}{2S+1} \sum_{L=0}^{2S} \sum_{M=-L}^{L} \langle Y_{L,M}^* \rangle(t) Y_{L,M}(\vartheta, \varphi), \tag{24}$$

where $\langle Y_{L,M}^* \rangle(t) = \frac{2S+1}{4\pi} \int Y_{L,M}^*(\vartheta, \varphi) W_S(\vartheta, \varphi, t) d\Omega$ and $Y_{L,M}^* = (-1)^M Y_{L,-M}$. Equation (24) obviously emphasizes the relationship with the conventional infinite series representation of the relevant classical Boltzmann distribution.

By writing the reduced density matrix evolution equation (4) in terms of the inverse transformation (22) we then have *implicitly* in terms of the corresponding phase space distribution $W_S(\vartheta, \varphi, t)$ which essentially represents a mapping of (4) onto phase space

$$\int \hat{w}_1 \frac{\partial W_S}{\partial t} d\Omega = -\frac{i}{\hbar} \int [\hat{H}_S, \hat{w}_1] W_S d\Omega + \int \mathrm{St}\{\hat{w}_1\} W_S d\Omega. \tag{25}$$

The right-hand side of (25) is not yet however in the form of an inverse Wigner-Stratononvich map as dictated by (22). Hence these terms for a given spin Hamiltonian must first be written as the inverse of such a map with kernel $\hat{w}_1$. Then an explicit phase space master equation may be immediately extracted from the definition of the transformation (22) and from the result for the collision kernel (17) and (18). This is accomplished by writing the commutators of both the deterministic and collision kernel terms as differential operators acting on the Wigner distribution for spins W_S *in a manner such that after integration by parts* $\hat{w}_1$ *appears as the kernel of the transformation*. We remark that although the procedure in determining the evolution equation for the Wigner function for spins is formally similar to that for point particles undergoing translational motion, the problem for spins is inherently much more difficult as the evolution equation for a given spin Hamiltonian must by derived in *each* particular case. As far as axially symmetric problems are concerned, a detailed derivation has already been given in Ref. [16] for the axially symmetric problem of a uniaxial paramagnet in a uniform field parallel to the anisotropy axis. We shall now generalize the results of that paper to treat the present nonaxially symmetric problem using the rotated coordinate system described above.

Now, in the explicit transformation of the density matrix evolution equation into phase space we need the relation between the polarization operators $\hat{T}_{L,M}^{(S)}$ and the spin operators $\hat{S}_\mu$ embodied in their commutator relation, namely, [46]

$$[\hat{S}_\mu, \hat{T}_{L,M}^{(S)}] = \sqrt{L(L+1)} C_{L,M,1,\mu}^{L,M+\mu} \hat{T}_{L,M+\mu}^{(S)}. \tag{26}$$

Furthermore, we also need the fact that the spherical components $\hat{L}_\mu$ of the angular momentum operator $\hat{\mathbf{L}} = (\hat{L}_{+1}, \hat{L}_0, \hat{L}_{-1})$ defined as [46]

$$\hat{L}_0 = -i \frac{\partial}{\partial \varphi}, \qquad \hat{L}_{\pm 1} = -\frac{1}{\sqrt{2}} e^{\pm i\varphi} \left(\frac{\partial}{\partial \vartheta} \pm i \cot\vartheta \frac{\partial}{\partial \varphi} \right), \tag{27}$$

act on the complex conjugate of the spherical harmonics $Y_{L,M}^*(\vartheta, \varphi)$ as [46]

$$\hat{L}_\mu Y_{L,M}^* = -\sqrt{L(L+1)} C_{L,M,1,\mu}^{L,M+\mu} Y_{L,M+\mu}^*. \tag{28}$$

Hence, (26) and (28) with the Wigner-Stratonovich kernel (23) yield an identity for the commutator, viz.

$$[\hat{S}_\mu, \hat{w}_1] = -\hat{L}_\mu \hat{w}_1. \tag{29}$$

This result can now be used to map the commutators in (25) to differential operators acting in phase space. Next to find explicitly the terms $\hat{S}_\mu \hat{w}_1$ and $\hat{w}_1 \hat{S}_\mu$ (which arise from $\hat{H}_S$) involved in the commutators in (25), one must expand the operator $\hat{S}_\mu \hat{T}^{(S)}_{L,M}$ as a sum of polarization operators using (11) and the product formula of these operators, namely, [46]

$$\hat{T}^{(S)}_{L_1,M_1}\hat{T}^{(S)}_{L_2,M_2} = \sum_{L=0}^{2S}(-1)^{2S+L}\sqrt{(2L_1+1)(2L_2+1)}\begin{Bmatrix} L_1 & L_2 & L \\ S & S & S \end{Bmatrix} C^{L,M}_{L_1,M_1,L_2,M_2}\hat{T}^{(S)}_{L,M}, \tag{30}$$

where $\left\{\begin{smallmatrix} L_1 & L_2 & L \\ S & S & S \end{smallmatrix}\right\}$ is Wigner's $6j$-symbol [46]. Now both the Wigner-Stratonovich operator $\hat{w}_1$ and the Wigner distribution for spins W_S may be expanded as *finite* linear combinations ($L = 0 \to 2S$) of polarization operators and spherical harmonics respectively; see (23) and (24). This property, the bijective nature of the transformation, and the orthogonality relations of the spherical harmonics along with (29) and (30) now yield

$$\int W_S \hat{S}_0 \hat{w}_1 d\Omega = \frac{1}{2}\int W_S\left[2(S+1)\cos\vartheta + \sin\vartheta\frac{\partial}{\partial\vartheta} - \hat{L}_0\right]\hat{w}_1 d\Omega \tag{31}$$

and

$$\int W_S \hat{S}_{\pm1} \hat{w}_1 d\Omega = -\frac{1}{2}\int W_S\left[(1\pm\cos\vartheta)\hat{L}_{\pm1} + \frac{1}{\sqrt{2}}\sin\vartheta e^{\pm i\varphi}(\hat{L}_0 \pm 2(S+1))\right]\hat{w}_1 d\Omega. \tag{32}$$

Following integrating by parts (see Appendix B of Ref. [16]), the above relations become explicit inverse Wigner-Stratonovich transformations showing how the $\hat{S}_\mu \hat{w}_1$ involved in the commutators are related to their analogues in phase space. We can also represent the transformation given by (31) and (32) in vector form as

$$\hat{\mathbf{S}}\hat{\rho}(t) = \frac{2S+1}{4\pi}\int W_S\left[(S+1)\mathbf{u} - \frac{1}{2}(\nabla + \hat{\mathbf{L}})\right]\hat{w}_1 d\Omega \tag{33}$$

which shows (again after integrating by parts) how $\hat{\mathbf{S}}\hat{\rho}(t)$ may be represented as a pure inverse Wigner-Stratonovich transformation. Here the various vectors and operators are [46]

$$\mathbf{u} = (u_{+1}, u_0, u_{-1}), \qquad u_{\pm1} = \mp\sin\vartheta e^{\pm i\varphi}/\sqrt{2}, \qquad u_0 = \cos\vartheta,$$

$$\nabla = (\nabla_{+1}, \nabla_0, \nabla_{-1}), \qquad \nabla_{\pm1} = \mp\frac{e^{\pm i\varphi}}{\sqrt{2}}\left(\cos\vartheta\frac{\partial}{\partial\vartheta} \pm i\frac{1}{\sin\vartheta}\frac{\partial}{\partial\varphi}\right), \qquad \nabla_0 = -\sin\vartheta\frac{\partial}{\partial\vartheta}.$$

In like manner the integral relations corresponding to the terms $\hat{w}_1 \hat{S}_\mu$ in the commutator are easily obtained using (29), so that they take the form

$$\int W_S \hat{w}_1 \hat{S}_\mu d\Omega = \int W_S(\hat{S}_\mu + \hat{L}_\mu)\hat{w}_1 d\Omega. \tag{34}$$

Equation (34) can also be represented in vector form as

$$\hat{\rho}(t)\hat{\mathbf{S}} = \frac{2S+1}{4\pi}\int W_S\left[(S+1)\mathbf{u} - \frac{1}{2}(\nabla - \hat{\mathbf{L}})\right]\hat{w}_1 d\Omega. \tag{35}$$

Now noting (33) and (35), substituting (18) into (25), and using integration by parts to reduce them to pure inverse Wigner-Stratonovich transformations (again as in Appendix B of [16]), we ultimately have the vector-valued master equation (which is the desired phase space evolution equation corresponding to (4) with the collision kernel (18))

$$\frac{\partial W_S}{\partial t} - i\frac{\xi}{\hbar\beta}(\hat{\mathbf{L}}\cdot\mathbf{u}_H^{\dagger})W_S$$
$$= \frac{1}{2}(\hat{\mathbf{L}}\mathbf{A})\mathbf{D}\left\{\mathbf{E}'^{\xi}_{+}[(\nabla+\hat{\mathbf{L}}+2S\mathbf{u})\mathbf{A}]^{\dagger} - \mathbf{E}'^{\xi}_{-}[(\nabla-\hat{\mathbf{L}}+2S\mathbf{u})\mathbf{A}]^{\dagger}\right\}W_S, \quad (36)$$

where the matrix $\mathbf{A}$ and the diffusion tensor $\mathbf{D}$ are defined by (9) and (15), respectively, and

$$\mathbf{E}'^{\xi}_{\pm} = \begin{pmatrix} e^{\xi}\delta_{1,\pm1}+\delta_{1,\mp1} & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & e^{\xi}\delta_{1,\mp1}+\delta_{1,\pm1} \end{pmatrix}.$$

The vector valued master equation in phase space, (36), for the nonaxially symmetric problem of a uniform field of arbitrary direction can also obviously be presented in coordinate terms avoiding vector differential operators altogether. These expressions are explicitly given in Appendix B.

4 Properties of the Master Equation in Phase Space

The stationary phase space distribution function $W_S^{eq}(\vartheta,\varphi)$ corresponding to the canonical density matrix $\hat{\rho}_{eq} = e^{-\beta H_S}/Z_S$ is given by [40]

$$W_S^{eq}(\vartheta,\varphi) = Z_S^{-1}[\cosh(\xi/2)+\sinh(\xi/2)(\mathbf{u}\cdot\mathbf{u}_H^{\dagger})]^{2S}, \quad (37)$$

where

$$(\mathbf{u}\cdot\mathbf{u}_H^{\dagger}) = \sin\vartheta\cos\varphi\sin\vartheta_H\cos\varphi_H + \sin\vartheta\sin\varphi\sin\vartheta_H\sin\varphi_H + \cos\vartheta\cos\vartheta_H$$

and

$$Z_S = \frac{2S+1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\left[\cosh(\xi/2)+\sinh(\xi/2)(\mathbf{u}\cdot\mathbf{u}_H^{\dagger})\right]^{2S}\sin\vartheta\, d\vartheta\, d\varphi$$
$$= \sinh\left[(S+1/2)\,\xi\right]/\sinh(\xi/2)$$

is the partition function. Because of our ansatz that the stationary solution of (13) is the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta\hat{H}_S}/Z_S$, the phase space distribution $W_S^{eq}(\vartheta,\varphi)$ from (37) is the stationary solution of the master equation (36). In the classical limit, $\beta\to 0$, $S\to\infty$, and $\beta S = \text{const}$, the distribution $W_S^{eq}(\vartheta,\varphi)$ tends to the Boltzmann distribution, i.e.,

$$\frac{2S+1}{4\pi}W_S^{eq}(\vartheta,\varphi) \to \frac{1}{Z_{cl}}e^{-\beta V(\vartheta,\varphi)},$$

where $\beta V(\vartheta,\varphi) = -\xi'(\mathbf{u}\cdot\mathbf{u}_H^{\dagger})$ is the normalized free energy, $\xi' = \xi S$, and $Z_{cl} = \int_0^{\pi}\int_0^{2\pi} e^{-\beta V(\vartheta,\varphi)}\sin\vartheta\, d\vartheta\, d\varphi$ is the classical partition function.

The phase space master equation (36) may be compared with previous results. First, we consider a field applied along the Z-axis (i.e., the source coordinates are $\vartheta_H = \varphi_H = 0$) so that (36) reduces to

$$\frac{\partial W_S}{\partial t} = \frac{\xi}{\hbar\beta}\frac{\partial W_S}{\partial\varphi} + D_\parallel \frac{\partial^2 W_S}{\partial\varphi^2} + D_\perp \frac{e^\xi - 1}{2\sin\vartheta}\left[\cot\vartheta[\cos\vartheta\coth(\xi/2) + 1]\frac{\partial^2 W_S}{\partial\varphi^2}\right.$$
$$\left. + \frac{\partial}{\partial\vartheta}\left(2S\sin^2\vartheta\, W_S + \sin\vartheta[\coth(\xi/2) + \cos\vartheta]\frac{\partial W_S}{\partial\vartheta}\right)\right]. \quad (38)$$

This equation is simply that of Shibata and co-workers [7] obtained using the generalized coherent states formalism which they transferred to the spherical polar coordinate representation. In the classical limit, $\beta \to 0$, $S \to \infty$, $\xi' = \xi S = \text{const}$, (36) reduces to the relevant Fokker-Planck equation describing the rotational diffusion of a classical spin, namely,

$$\frac{\partial W}{\partial t} + i\frac{\gamma}{\mu}\mathbf{u}\cdot(\nabla W \times \nabla V)^\dagger = \beta D_\perp \nabla(W\nabla^\dagger V) + (\hat{\mathbf{L}}\mathbf{A})\mathbf{D}(\hat{\mathbf{L}}\mathbf{A})^\dagger W, \quad (39)$$

where $\nabla = -\mathbf{e}_{+1}\nabla_{-1} + \mathbf{e}_0\nabla_0 - \mathbf{e}_{-1}\nabla_{+1}$ is the gradient operator, $\mathbf{e}_{+1}, \mathbf{e}_0, \mathbf{e}_{-1}$ are the covariant spherical basis vectors [46], and $\mu = \gamma\hbar S$ is the magnetic moment associated with the spin. Here we have used the following limits

$$\lim_{S\to\infty}\frac{\xi}{\hbar\beta}\left(\hat{\mathbf{L}}\cdot\mathbf{u}_H^\dagger\right)W_S = -\frac{\gamma}{\mu}\mathbf{u}\cdot(\nabla W \times \nabla V),$$

$$\lim_{S\to\infty}(\hat{\mathbf{L}}\mathbf{A})\mathbf{D}\left[\left(\mathbf{E}_+^{\prime\xi} + \mathbf{E}_-^{\prime\xi}\right)(\hat{\mathbf{L}}\mathbf{A})^\dagger\right]W_S = 2(\hat{\mathbf{L}}\mathbf{A})\mathbf{D}(\hat{\mathbf{L}}\mathbf{A})^\dagger W,$$

$$\lim_{S\to\infty}(\hat{\mathbf{L}}\mathbf{A})\mathbf{D}\left[\left(\mathbf{E}_+^{\prime\xi} - \mathbf{E}_-^{\prime\xi}\right)(\nabla\mathbf{A})^\dagger\right]W_S = 0$$

and

$$\lim_{S\to\infty} S(\hat{\mathbf{L}}\mathbf{A})\mathbf{D}[(\mathbf{E}_+^{\prime\xi} - \mathbf{E}_-^{\prime\xi})(\mathbf{u}\mathbf{A})^\dagger]W_S = \beta D_\perp\nabla(W\nabla^\dagger V).$$

Equation (39) simplifies for an isotropic spin diffusion ($D_\perp = D_\parallel$) to give

$$\frac{\partial W}{\partial t} + i\frac{\gamma}{\mu}\mathbf{u}\cdot(\nabla W \times \nabla V)^\dagger = D_\perp[\beta\nabla(W\nabla^\dagger V) + \Delta W], \quad (40)$$

where

$$\Delta = \nabla\cdot\nabla^\dagger = \frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}\right) + \frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial\varphi^2}$$

is the angular part of the Laplacian operator.

5 Concluding Remarks

We have shown via a rotation of the coordinate system how one may derive a vector valued master equation (36) for the time evolution of the phase space distribution function of the simplest nonaxially symmetric spin system, namely a spin in an arbitrary directed uniform field in contact with a thermal bath at temperature T. We have assumed throughout that the weak spin-bath coupling limit applies and that the correlation time characterizing the bath is so short that the stochastic process originating in it is Markovian. Thus we have frequency independent damping. The derivation of the master equation for the density matrix was accomplished by first representing our spin system Hamiltonian in a new coordinate system where the uniform magnetic field is directed along the new Z' axis so that only the diagonal terms participate in the time evolution [17]. It is then possible to return to the original coordinate system using the properties of the Wigner D functions. Thus the nonaxially symmetric problem has been effectively reduced to the solution of the axially symmetric problem of the spin relaxation in a field applied along the Z' axis of the new coordinate system. The solution of the axially symmetric problem, allowing one to determine the relaxation of the magnetization as a function of spin size S, has been considered in detail in Refs. [7, 10, 15–17] using both the phase space master equation and reduced density matrix formulations. Each method yields exactly the same results for the magnetization and its characteristic times although they have outwardly very different forms. Thus by virtue of the rotation of the coordinate system the derivation of the nonaxially symmetric phase space master equation is then effectively reduced to the evaluation of the various commutators pertaining to the axially symmetric problem, in the new coordinate system. Hence, the phase space master equation may be determined as before [7, 10, 15] by writing the reduced density matrix master equation (4) with kernel (18) in terms of the inverse Wigner-Stratonovich transformation (22) and then explicitly writing the various commutators as differential operators acting on the phase space distribution in a manner such that after integration by parts $\hat{w}_1$ appears as the kernel of the transformation. This reduction of the commutators to their equivalent forms in phase space is accomplished using various properties of the spherical components of the spin operator, the polarization operators, the spherical harmonics and the angular momentum operator. Hence we have derived the master equation, in the compact vector form (36). A particular advantage of that form is that it is now relatively easy to visualize how a new approach to nonaxially symmetrical problems by using a representation in which only the diagonal terms in the density matrix contribute to the time evolution, may be applied to more complicated situations. Examples are those posed by the Hamiltonian

$$\beta \hat{H}_S = -\xi \hat{S}_X - \sigma \hat{S}_Z^2 \tag{41}$$

for a uniaxial spin system in a transverse field (known otherwise as the Lipkin-Meshkov Hamiltonian [53, 54]) and those pertaining to biaxial and mixed anisotropy, namely

$$\beta \hat{H}_S = -\sigma \hat{S}_Z^2 + \delta(\hat{S}_X^2 - \hat{S}_Y^2), \tag{42}$$

$$\beta \hat{H}_S = -\sigma_1 \hat{S}_Z^2 - \sigma_2 \hat{S}_Z^4 + \chi(\hat{S}_+^4 + \hat{S}_-^4). \tag{43}$$

We note that $\hat{H}_S$ from (42) and (43) is commonly used to describe the magnetic properties of an octanuclear iron(III) molecular cluster Fe8 and the dodecanuclear manganese molecular cluster Mn12 [55], etc.

Having formulated the appropriate master equations in representation space for quantum spin systems (molecular magnets, nanoclusters, etc.), these can be solved for the magnetization, dynamic susceptibility, switching field curves, hysteresis loops, etc. This can be accomplished using the powerful matrix continued fraction method originally developed [30] in the context of the Brown theory of reversal of the magnetization by thermal agitation for classical superparamagnets [50, 51]. Here a very efficient method of solution of the corresponding Fokker-Planck equation for the distribution function of the magnetization vector orientation governing the stochastic dynamics of a classical spin comprises the determination of the statistical moments [expectation values of the spherical harmonics $\langle Y_{L,M}\rangle(t)$]. These in general satisfy differential-recurrence relations and allow one to evaluate desired observables [30]. This method can also be applied to the quantum problem. The reason is that the phase-space distribution $W_S(\vartheta, \varphi, t)$ may be presented for arbitrary S in terms of a finite linear combination of the spherical harmonics, namely, (24), which is valid for an *arbitrary* spin system. The differential-recurrence relations for $\langle Y_{L,M}\rangle(t)$ can be obtained [17] by substituting the distribution function $W_S(\vartheta, \varphi, t)$ from (24) into the master equation (20) so that the latter becomes

$$\frac{d}{dt}\langle Y_{L,M}\rangle(t) = \sum_{L',M'} b_{L,M}^{L',M'} \langle Y_{L',M'}\rangle(t), \tag{44}$$

where $b_{L,M}^{L',M'}$ are the Fourier coefficients which depend on the precise form of the Hamiltonian. In particular, solving (44) for $\langle Y_{1,0}\rangle(t)$ and $\langle Y_{1,\pm1}\rangle(t)$ and noting the correspondence rules of the spin operators $\hat{S}_X$, $\hat{S}_Y$, $\hat{S}_Z$ and Weyl symbols S_X, S_Y, S_Z in the phase space [40], one can calculate the longitudinal, $\langle\hat{S}_Z\rangle(t)$, and transverse, $\langle\hat{S}_\pm\rangle(t) = \langle\hat{S}_X\rangle(t) \pm i\langle\hat{S}_Y\rangle(t)$ components of the magnetization as [17]

$$\langle\hat{S}_\pm\rangle(t) = \mp\sqrt{8\pi/3}(S+1)\langle Y_{1,\pm1}\rangle(t) \quad \text{and} \quad \langle\hat{S}_Z\rangle(t) = \sqrt{4\pi/3}(S+1)\langle Y_{1,0}\rangle(t).$$

Equation (44) has been encountered in the theory of the magnetization relaxation of classical spins [30] and can be solved either by direct matrix diagonalization, involving the calculation of the eigenvalues and eigenvectors of the system matrix, or by the computationally efficient (matrix) continued fraction method [30, 31]. Just as in the classical case, having solved (44), one could study the transition of the relaxation from that of an elementary spin ($S \sim 1$) to molecular magnets ($S \sim 10$) to nanoclusters ($S \sim 100$), and to classical superparamagnetic particles ($S \geq 1000$). In particular, the results so obtained could then be compared with the asymptotic solutions yielded by quantum Kramers escape rate theory as extended to spins for the purpose of establishing simple analytic formulae for the reversal time as a function of S [47]. Thus one would have a complete quantum analogue of the Brown theory of magnetization relaxation [50, 51]. Furthermore, the results could also be compared as was previously done for the latter theory with suitable low temperature experimental observations of the escape rate and the associated susceptibilities of molecular magnets, nanoclusters, etc. These results would also allow one to include spin size effects in important technological applications of magnetic relaxation such as the reversal time of the magnetization, the hysteresis and switching field curves, etc. In particular one could evaluate the temperature dependence of the switching field curves and corresponding hysteresis loops via obvious spin size corrected generalizations of the known classical methods used in the analysis of the classical stochastic spin dynamics. The first steps in realization of this program have been recently accomplished in Refs. [17, 56] in the particular application to uniaxial superparamagnets. Results of its application to nonaxially symmetric spin systems (such as a quantum superparamagnet in the field applied at an angle with the anisotropy axis, etc.) will be published elsewhere.

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Appendix A: Derivation of (13)

In order to derive (13) for the reduced density matrix in the new coordinate system we must express all operators occurring in the master equation in terms of that coordinate system. The expression for the spin Hamiltonian in the new coordinate system is given by (12) while the spin-bath interaction Hamiltonian $\hat{H}_{SB}$ in that coordinate system is

$$\hat{H}_{SB} = -\hbar\gamma \sum_{\mu=-1}^{1} \hat{h}'^{\mu} \hat{S}'_{\mu}, \tag{A.1}$$

where $\hat{h}'^0 = \hat{h}'_Z$, and $\hat{h}'^{\pm1} = \mp(\hat{h}'_X \mp i\hat{h}'_Y)/\sqrt{2}$ are the (contravariant) spherical components of the vector operator $\hat{\mathbf{h}}'^{\dagger} = (h'^{*}_{+1}, h^{*}_{0}, h^{*}_{-1})^T = (h'^{+1}, h'^{0}, h'^{-1})^T$. Inserting the interaction Hamiltonian into (4), we have the expansion of the double commutator in (5), i.e., the collision kernel in our new coordinate system which can be written as

$$\begin{aligned}
\mathrm{St}\{\rho'(t)\} = \gamma^2 \int_0^\infty & \big\{\langle \hat{h}'^0(\tau)\hat{h}'^0\rangle\big[e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{S}'_0\hat{\rho}'(t)e^{-\frac{i\tau}{\hbar}\hat{H}'_S}, \hat{S}'_0\big] \\
&+ \langle \hat{h}'^0\hat{h}'^0(\tau)\rangle\big[\hat{S}'_0, e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{\rho}'(t)\hat{S}'_0 e^{-\frac{i\tau}{\hbar}\hat{H}'_S}\big] \\
&+ \langle \hat{h}'^{-1}(\tau)\hat{h}'^{+1}\rangle\big[e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{S}'_{+1}\hat{\rho}'(t)e^{-\frac{i\tau}{\hbar}\hat{H}'_S}, \hat{S}'_{-1}\big] \\
&+ \langle \hat{h}'^{+1}(\tau)\hat{h}'^{-1}\rangle\big[e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{S}'_{-1}\hat{\rho}'(t)e^{-\frac{i\tau}{\hbar}\hat{H}'_S}, \hat{S}'_{+1}\big] \\
&+ \langle \hat{h}'^{+1}\hat{h}'^{-1}(\tau)\rangle\big[\hat{S}'_{-1}, e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{\rho}'(t)\hat{S}'_{+1} e^{-\frac{i\tau}{\hbar}\hat{H}'_S}\big] \\
&+ \langle \hat{h}'^{-1}\hat{h}'^{+1}(\tau)\rangle\big[\hat{S}'_{+1}, e^{\frac{i\tau}{\hbar}\hat{H}'_S}\hat{\rho}'(t)\hat{S}'_{-1} e^{-\frac{i\tau}{\hbar}\hat{H}'_S}\big]\big\} d\tau.
\end{aligned} \tag{A.2}$$

Here the angular braces denote bath correlation functions, namely

$$\langle \hat{h}'^i(t_1)\hat{h}'^j(t_2)\rangle = Z_B^{-1}\,\mathrm{Tr}_B\big\{\hat{h}'^i(t_1)\hat{h}'^j(t_2)\hat{\rho}_B^{eq}\big\}, \tag{A.3}$$

where $\hat{h}'^{\mu}(\tau) = e^{i\hat{H}_B\tau/\hbar}\hat{h}'^{\mu}(0)e^{-i\hat{H}_B\tau/\hbar}$ with index $\mu = 0, \pm1$. Moreover, the cyclic property of trace, $\mathrm{Tr}\{ABC\} = \mathrm{Tr}\{CAB\}$, along with the following properties of the bath correlation functions (assuming axial symmetry about the Z'-axis and that the average of the white noise caused by the Brownian motion of the bath, is zero, i.e., $\langle \hat{\mathbf{h}}' \rangle = 0$) have been used

$$\langle \hat{h}'^{\mu}(t_1)\hat{h}'_{\nu}(t_2)\rangle = 0, \quad \mu \neq \nu. \tag{A.4}$$

Furthermore, the bath operators $\hat{h}'^{\mu}$, $e^{\pm i\hat{H}_B\tau/\hbar}$, $\hat{\rho}_B^{eq}$ commute with the system operators $\hat{S}'_{\mu}$, $e^{\pm i\hat{H}_S\tau/\hbar}$, $\hat{\rho}'$ but (generally) not with one another. We emphasize that the properties (A.4) are not valid in general for the coordinate system *XYZ* (the nonaxially symmetric problem) because of the anisotropic properties of the system (in our case the fact that the uniform field $\mathbf{H}$ is directed along the Z' axis distinguishes this from the other axes X' and Y'). Nevertheless, one can easily show that for an isotropic system

$$\langle \hat{h}'^{\mu}(t_1)\hat{h}'_{\nu}(t_2)\rangle = \langle \hat{h}^{\mu}(t_1)\hat{h}_{\nu}(t_2)\rangle = 0, \quad \mu \neq \nu.$$

Now by substituting the Hamiltonian $\hat{H}'_S$ in the rotated system (12) into (A.2) and taking account of the operator identity (19), we can further simplify (A.2) to yield

$$\begin{aligned}\mathrm{St}\{\rho'(t)\} = \gamma^2 \int_0^\infty \Big\{ &\langle \hat{h}'^0(\tau)\hat{h}'^0\rangle\big[\hat{S}'_0\hat{\rho}'(t), \hat{S}'_0\big] + \langle \hat{h}'^0\hat{h}'^0(\tau)\rangle\big[\hat{S}'_0, \hat{\rho}'(t)\hat{S}'_0\big] \\ &+ \langle \hat{h}'^{-1}(\tau)\hat{h}'^{+1}\rangle e^{-\frac{i\xi\tau}{\beta\hbar}}\big[\hat{S}'_{+1}\hat{\rho}'(t), \hat{S}'_{-1}\big] + \langle \hat{h}'^{+1}(\tau)\hat{h}'^{-1}\rangle e^{\frac{i\xi\tau}{\beta\hbar}}\big[\hat{S}'_{-1}\hat{\rho}'(t), \hat{S}'_{+1}\big] \\ &+ \langle \hat{h}'^{+1}\hat{h}'^{-1}(\tau)\rangle e^{-\frac{i\xi\tau}{\beta\hbar}}\big[\hat{S}'_{-1}, \hat{\rho}'(t)\hat{S}'_{+1}\big] \\ &+ \langle \hat{h}'^{-1}\hat{h}'^{+1}(\tau)\rangle e^{\frac{i\xi\tau}{\beta\hbar}}\big[\hat{S}'_{+1}, \hat{\rho}'(t)\hat{S}'_{-1}\big]\Big\} d\tau. \end{aligned} \tag{A.5}$$

Next in order to evaluate the averages of the noise terms, we introduce the one-sided Fourier transforms of the (bath) time correlation functions (see, for example, [57], §6.4), which can be defined as

$$\tilde{C}_B^0(\omega) = \gamma^2 \int_0^\infty \langle \hat{h}'^0(0)\hat{h}'^0(\tau)\rangle e^{i\omega\tau} d\tau \quad \text{and} \quad \tilde{C}_B(\omega) = \gamma^2 \int_0^\infty \langle \hat{h}'^{-1}(0)\hat{h}'^{+1}(\tau)\rangle e^{i\omega\tau} d\tau.$$

By noting the following property ($\hbar\omega + E_l = E_k$)

$$\begin{aligned} &e^{-\beta\hbar\omega}\int_0^\infty \langle \hat{h}^{+1}(\tau)\hat{h}^{-1}\rangle e^{i\omega\tau} d\tau \\ &\quad = Z_B^{-1} e^{-\beta\hbar\omega}\int_0^\infty \sum_{k,l} e^{iE_l\tau/\hbar} h_{lk}^{+1} e^{-iE_k\tau/\hbar} h_{kl}^{-1} e^{-\beta E_l} e^{i\omega\tau} d\tau \\ &\quad = Z_B^{-1}\int_0^\infty \sum_{k,l} e^{iE_l\tau/\hbar} h_{lk}^{+1} e^{-iE_k\tau/\hbar} h_{kl}^{-1} e^{-\beta E_k} e^{i\omega\tau} d\tau \\ &\quad = \int_0^\infty \langle \hat{h}^{-1}\hat{h}^{+1}(\tau)\rangle e^{i\omega\tau} d\tau, \end{aligned}$$

and assuming frequency independent damping, viz., $[\tilde{C}_B^0(\omega) = \tilde{C}_B^{0*}(\omega) \to D_\parallel$ and $\tilde{C}_B(\omega) = \tilde{C}_B^*(\omega) \to D_\perp]$ we then have from (A.5) the reduced density matrix evolution (13) in the new coordinate system.

Appendix B: Phase Space Master Equation in Spherical Polar Coordinates

The deterministic operator of (36) can be presented in spherical polar coordinates as

$$i(\hat{\mathbf{L}}\cdot\mathbf{u}_H^\dagger)W_S = -\sin(\varphi-\varphi_H)\sin\vartheta_H \frac{\partial W_S}{\partial\vartheta} + [\cos\vartheta_H - \sin\vartheta_H\cot\vartheta\cos(\varphi_H-\varphi)]\frac{\partial W_S}{\partial\varphi}.$$

The collision kernel is separated into a "parallel", $\mathrm{St}_\parallel\{W_S\}$, and "perpendicular", $\mathrm{St}_\perp\{W_S\}$, parts. The parallel part of the collision kernel is

$$\mathrm{St}_\parallel\{W_S\} = D_\parallel\left[\cos\vartheta_H\frac{\partial S^\parallel}{\partial\varphi} - \sin\vartheta_H\left(\sin(\varphi-\varphi_H)\frac{\partial S^\parallel}{\partial\vartheta} + \cos(\varphi-\varphi_H)\cot\vartheta\frac{\partial S^\parallel}{\partial\varphi}\right)\right],$$

where

$$S^{\parallel} = \cos\vartheta_H \frac{\partial W_S}{\partial\varphi} - \sin\vartheta_H \left(\sin(\varphi-\varphi_H)\frac{\partial W_S}{\partial\vartheta} + \cos(\varphi-\varphi_H)\cot\vartheta \frac{\partial W_S}{\partial\varphi}\right).$$

The perpendicular part of the collision kernel is

$$\begin{aligned}\mathrm{St}_{\perp}\{W_S\} = &-\frac{D_\perp}{2}\left(\cos(\varphi-\varphi_H)\frac{\partial S_1^{\perp}}{\partial\vartheta} - \sin(\varphi-\varphi_H)\cot\vartheta\frac{\partial S_1^{\perp}}{\partial\varphi}\right)\\ &-\frac{D_\perp}{2}\left[\cos\vartheta_H\left(\sin(\varphi-\varphi_H)\frac{\partial S_2^{\perp}}{\partial\vartheta} + \cos(\varphi-\varphi_H)\cot\vartheta\frac{\partial S_2^{\perp}}{\partial\varphi}\right) + \sin\vartheta_H\frac{\partial S_2^{\perp}}{\partial\varphi}\right],\end{aligned}$$

where

$$\begin{aligned}S_1^{\perp} = (1-e^{\xi})\Bigg[&\cos\vartheta_H\cos\vartheta\left(\cos(\varphi-\varphi_H)\frac{\partial W_S}{\partial\vartheta} - \sin(\varphi-\varphi_H)\cot\vartheta\frac{\partial W_S}{\partial\varphi}\right)\\ &-\cos\vartheta_H\sin\vartheta\left(\sin(\varphi-\varphi_H)\frac{\partial W_S}{\partial\varphi} - 2S\cos(\varphi-\varphi_H)W_S\right)\\ &+\sin\vartheta_H\left(-2S\cos\vartheta\, W_S + \sin\vartheta\frac{\partial W_S}{\partial\vartheta}\right)\Bigg]\\ &-(1+e^{\xi})\left[\cos(\varphi-\varphi_H)\frac{\partial W_S}{\partial\vartheta} - \sin(\varphi-\varphi_H)\cot\vartheta\frac{\partial W_S}{\partial\varphi}\right]\end{aligned}$$

and

$$\begin{aligned}S_2^{\perp} = (1-e^{\xi})\Bigg[&\cos\vartheta\left(\sin(\varphi-\varphi_H)\frac{\partial W_S}{\partial\vartheta} + \cos(\varphi-\varphi_H)\cot\vartheta\frac{\partial W_S}{\partial\varphi}\right)\\ &+\sin\vartheta\left(\cos(\varphi-\varphi_H)\frac{\partial W_S}{\partial\varphi} + 2S\sin(\varphi-\varphi_H)W_S\right)\Bigg]\\ &-(1+e^{\xi})\left[\cos\vartheta_H\left(\sin(\varphi-\varphi_H)\frac{\partial W_S}{\partial\vartheta} + \cos(\varphi-\varphi_H)\cot\vartheta\frac{\partial W_S}{\partial\varphi}\right) + \sin\vartheta_H\frac{\partial W_S}{\partial\varphi}\right].\end{aligned}$$

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