J Stat Phys (2008) 131: 969–987
DOI 10.1007/s10955-008-9522-2

Master Equation in Phase Space for a Uniaxial Spin System

Yuri P. Kalmykov · William T. Coffey · Serguey V. Titov

Received: 25 December 2007 / Accepted: 7 March 2008 / Published online: 26 March 2008

Abstract A master equation, for the time evolution of the quasi-probability density function of spin orientations in the phase space representation of the polar and azimuthal angles is derived for a uniaxial spin system subject to a magnetic field parallel to the axis of symmetry. This equation is obtained from the reduced density matrix evolution equation (assuming that the spin-bath coupling is weak and that the correlation time of the bath is so short that the stochastic process resulting from it is Markovian) by expressing it in terms of the inverse Wigner-Stratonovich transformation and evaluating the various commutators via the properties of polarization operators and spherical harmonics. The properties of this phase space master equation, resembling the Fokker-Planck equation, are investigated, leading to a finite series (in terms of the spherical harmonics) for its stationary solution, which is the equilibrium quasi-probability density function of spin "orientations" corresponding to the canonical density matrix and which may be expressed in closed form for a given spin number. Moreover, in the large spin limit, the master equation transforms to the classical Fokker-Planck equation describing the magnetization dynamics of a uniaxial paramagnet.

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

Y.P. Kalmykov (✉)
Laboratoire de Mathématiques, Physique et Systèmes, Université de Perpignan, 52, Avenue de Paul Alduy, 66860 Perpignan Cedex, France
e-mail: kalmykov@univ-perp.fr

W.T. Coffey · S.V. Titov
Department of Electronic and Electrical Engineering, Trinity College, Dublin 2, Ireland

S.V. Titov
Institute of Radio Engineering and Electronics, Russian Acad. Sci., Vvedenskii Square 1, Fryazino 141190, Russia

1 Introduction

Phase-space representations of quantum mechanical evolution equations provide a formal means of treating quantum effects in dynamical systems linking to the classical representations, thus allowing one to calculate quantum corrections to classical distribution functions [1, 2]. These representations (generally based on the coherent state representation of the density matrix introduced by Glauber and Sudarshan and widely used in quantum optics [2, 3]) when applied to spin systems (e.g., [4–13]) allow one to analyze 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 polar and azimuthal angles, constituting the canonical variables. The 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 [5–7, 13]. The phase space distribution function for spins was originally introduced by Stratonovich [14] for closed systems and further developed both for closed and open spin systems [8–24]. It is entirely analogous to the translational Wigner distribution $W(x,p,t)$ in the phase space of positions and momenta (x,p) [1, 25], 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. The phase space distribution 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) function $A(\vartheta,\varphi)$ so that quantum mechanical averages involving the density matrix may be calculated just as classical ones which is naturally suited to the calculation of quantum corrections to them [2]. The formalism is easy to implement because master equations governing the time evolution of phase space distributions enable 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. [26, 27]) to be seamlessly carried over into the quantum domain [13, 28–31].

Many quantum, semiclassical, and classical methods for the description of spin dynamics already exist, e.g., the reduced density matrix [32, 33], the stochastic Liouville equation [8, 9, 34], the Langevin equation [27], besides the phase space (generalized coherent state) [4–12] treatment. In general, however, phase space methods allow us to map quantum mechanical evolution equations for the (reduced) density matrix for spins onto a c-number space. These have an obvious advantage over the operator equations when one wishes to study the quantum/classical divide since the phase space representation of the density operator, is rendered in powers of Planck's constant or the inverse spin value. Nevertheless, phase space methods for spins have been usually applied in quantum optics and very little attention has been paid to any other spin systems. For example, explicit master equations for the phase space distribution function $W(\vartheta,\varphi,t)$ are available only for a spin $\mathbf{S}$ in a uniform magnetic field $\mathbf{H}$ [5, 6, 8–13] excluding anisotropy. Here as an explicit example of the phase space formalism in the magnetic context, we consider a uniaxial paramagnet of arbitrary spin value S in an external *constant* magnetic field $\mathbf{H}$ applied along the Z axis, i.e., the axis of symmetry, so that the Hamiltonian is

$$\beta\hat{H}_S = -\xi\hat{S}_Z - \sigma\hat{S}_Z^2, \tag{1}$$

where $\hat{S}_Z$ is the Z-component of the spin operator $\hat{\mathbf{S}}$, $\xi = \hbar\beta\gamma H_0$ is the precession (Larmor) frequency, γ is the gyromagnetic ratio, σ is the anisotropy constant, and $\beta = 1/(kT)$ is the inverse thermal energy. We remark in passing that Garanin and García-Palacios et al. [35–37] have treated the dynamics of an uniaxial paramagnet in a uniform field by proceeding from the quantum Hubbard operator representation of the evolution equation for the spin density matrix so that the phase space approach is complementary to theirs.

The paper is arranged as follows. In Sect. 2 we derive a master equation for a reduced density matrix for a spin system with Hamiltonian (1) in contact with a thermal bath. Next in Sect. 3, we present the basic phase space formalism and in Sect. 4, by expressing the reduced density matrix master equation as an inverse Wigner transform, we obtain the corresponding master equation for the phase space distribution $W(\vartheta, \varphi, t)$. In Sect. 5, we study general properties of the phase space master equation; in particular we show that in the limit $\sigma \to 0$, the equation reduces to that of Takahashi and Shibata [5, 6]. In Sect. 6, we discuss stationary and nonstationary solutions of the master equation in phase space. The mathematical details of the derivation are presented in the Appendices.

2 Evolution Equation for the Reduced Density Matrix

The equation of motion for the density matrix $\hat{\rho}_{SB}(t)$ of a spin system in contact with a heat bath may be written in the form of the Liouville equation [8, 9, 34]

$$\frac{\partial}{\partial t}\hat{\rho}_{SB}(t) = -\frac{i}{\hbar}[\hat{H}, \hat{\rho}_{SB}(t)] = -\frac{i}{\hbar}L\hat{\rho}_{SB}(t), \tag{2}$$

where $L = L_S + L_{SB} + L_B$ is the Liouville operator corresponding to the Hamiltonian $\hat{H}$ defined as

$$\hat{H} = \hat{H}_S + \hat{H}_{SB} + \hat{H}_B, \tag{3}$$

with $\hat{H}_S$ given by (1). The term $\hat{H}_B$ characterizes the bath and the term describing the spin-bath interaction can be written as $\hat{H}_{SB} = -\hbar\gamma\hat{\mathbf{h}} \cdot \hat{\mathbf{S}}$, where $\hat{\mathbf{h}}$ is the operator characterizing the collision damping (due to the bath) incurred by the precessional motion of the spin.

By using the projection operator technique [8, 9, 34], one can separate (2) for the evolution of the entire system into two distinct equations describing the evolution of the spin (S) and that of the bath (B), viz.

$$\wp\frac{\partial}{\partial t}\hat{\rho}_{SB} = -\frac{i}{\hbar}\wp L\hat{\rho}_{SB} = -\frac{i}{\hbar}\wp L\wp\hat{\rho}_{SB} - \frac{i}{\hbar}\wp L(1-\wp)\hat{\rho}_{SB},$$

$$(1-\wp)\frac{\partial}{\partial t}\hat{\rho}_{SB} = -\frac{i}{\hbar}(1-\wp)L\hat{\rho}_{SB} = -\frac{i}{\hbar}(1-\wp)L\wp\hat{\rho}_{SB} - \frac{i}{\hbar}(1-\wp)L(1-\wp)\hat{\rho}_{SB},$$

where the projection operator $\wp$ is defined as $\wp X = \hat{\rho}_B^{eq} Z_B^{-1}\mathrm{Tr}_B\{X\}$, $\hat{\rho}_B^{eq}$ is the equilibrium density matrix for the bath, and Z_B is the corresponding partition function. The reduced density matrix $\hat{\rho}(t) = \mathrm{Tr}_B\{\hat{\rho}_{SB}(t)\}$ has equation of motion

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\hbar^{-1}L_S\hat{\rho}(t) + \int_{-\infty}^{t}\Phi(t-\tau)\hat{\rho}(\tau)d\tau + \Psi(t), \tag{4}$$

where $L_S = Z_B^{-1}\mathrm{Tr}_B\{L\hat{\rho}_B^{eq}\}$ and

$$\Phi(t) = -(\hbar^2 Z_B)^{-1}\mathrm{Tr}_B\{Le^{-i(1-\wp)Lt/\hbar}(1-\wp)L\hat{\rho}_B^{eq}\},$$

$$\Psi(t) = -i\hbar^{-1}\mathrm{Tr}_B\{Le^{-i(1-\wp)Lt/\hbar}(1-\wp)\hat{\rho}(-\infty)\}.$$

The reduced master equation (4) may be further simplified when the interactions between the system and the bath are weak so that [8, 9, 34]

$$\frac{\partial}{\partial t}\hat{\rho}(t) = -i\hbar^{-1}L_S\hat{\rho}(t) - (\hbar^2 Z_B)^{-1}\mathrm{Tr}_B\left\{L_{SB}\int_0^\infty e^{-i(L_S+L_B)\tau/\hbar}L_{SB}\hat{\rho}_B^{eq}d\tau\,\hat{\rho}(t)\right\}. \quad (5)$$

Noting the explicit form of the Hamiltonian (3), we find that in the weak coupling limit, the reduced density matrix $\hat{\rho}$ now satisfies the equation (see Appendix A)

$$\frac{\partial\hat{\rho}}{\partial t} - \frac{i}{\hbar\beta}\{\sigma[\hat{S}_0^2, \hat{\rho}] + \xi[\hat{S}_0, \hat{\rho}]\} = \mathrm{St}(\hat{\rho}), \quad (6)$$

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

$$\begin{aligned}\mathrm{St}(\hat{\rho}) = D_\perp\{&[\hat{S}_+e^{2\sigma\hat{S}_0+(\sigma+\xi)\hat{I}}\hat{\rho}, \hat{S}_-] + [\hat{S}_+, e^{2\sigma\hat{S}_0+(\sigma+\xi)\hat{I}}\hat{\rho}\hat{S}_-]\\ &+ [\hat{S}_-\hat{\rho}, \hat{S}_+] + [\hat{S}_-, \hat{\rho}\hat{S}_+]\} + D_\parallel([\hat{S}_0\hat{\rho}, \hat{S}_0] + [\hat{S}_0, \hat{\rho}\hat{S}_0]),\end{aligned} \quad (7)$$

$\hat{S}_0 = \hat{S}_Z$, $\hat{S}_\pm = \hat{S}_X \pm i\hat{S}_Y$, and $\hat{I}$ is the identity matrix. Equation (7) with $\sigma = 0$ yields the known result (see, e.g., Refs. [5, 6, 8, 9, 38]) for a spin in a uniform magnetic field discounting anisotropy so that $\beta\hat{H}_S = -\xi\hat{S}_Z$. Explicit equations for the "diffusion" coefficients $D_\parallel$ and $D_\perp$ are given in Appendix A. Equation (6) effectively describes the evolution of the spin system in thermal contact with the bath at temperature T. The most important property of this collision kernel operator (7) is that the equilibrium spin density matrix

$$\hat{\rho}_{eq} = e^{-\beta\hat{H}_S}/\mathrm{Tr}\{e^{-\beta\hat{H}_S}\} \quad (8)$$

renders the collision kernel equal to zero, i.e., $\mathrm{St}(\hat{\rho}_{eq}) = 0$. Equation (6) 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. Conditions for the validity of the reduced density matrix evolution (6) are discussed in detail elsewhere (see, e.g., [5, 6, 38]). Essentially, (6) implies that the interactions between the spin and the heat bath are small enough to ensure the weak coupling limit and the correlation time characterizing the bath is so short that the stochastic process originating in the bath is Markovian [5, 6, 38]. Thus one may assume frequency independent damping. This approximation may be used in the high temperature limit. In the parameter range, where such an approximation is invalid (e.g., throughout the very low temperature region), a more general form of the master equation with time dependent diffusion coefficients [8, 9] should be used. We have chosen the frequency independent damping approximation because our objective is merely to understand in a semiclassical fashion how quantum effects alter the rotational Brownian motion and longitudinal relaxation of a classical dipole moment in an uniaxial anisotropy and Zeeman energy potential. We now proceed to the phase space representation of (6).

3 Phase-Space Formalism

The formal solution of the operator master equation (6) can be written using the irreducible tensor (polarization) operators $\hat{T}^{(S)}_{L,M}$ [33] as

$$\hat{\rho}(t) = \sum_{L=0}^{2S} \sum_{M=-L}^{L} a_{L,M}(t), \tag{9}$$

where the matrix elements of $\hat{T}^{(S)}_{L,M}$ are

$$[\hat{T}^{(S)}_{L,M}]_{m',m} = \sqrt{\frac{2L+1}{2S+1}} C^{S,m'}_{S,m,L,M}, \tag{10}$$

and $C^{S,m'}_{S,m,L,M}$ are the Clebsch-Gordan coefficients [39]. Equation (9) constitutes the expansion of the density matrix in terms of the polarization operators. Here the (scalar) coefficients $a_{L,M}(t)$ are the averages of the polarization operators $\langle \hat{T}^{(S)}_{L,M} \rangle(t) = \mathrm{Tr}\{\hat{\rho}(t)\hat{T}^{(S)}_{L,M}\}$, viz.,

$$a_{L,M}(t) = (-1)^M \langle \hat{T}^{(S)}_{L,-M} \rangle(t) = \langle \hat{T}^{(S)*}_{L,M} \rangle(t), \tag{11}$$

$$\langle \hat{T}^{(S)}_{L,M} \rangle(t) = \sqrt{\frac{2L+1}{2S+1}} \sum_{m,m'=-S}^{S} C^{S,m'}_{S,m,L,M} \rho_{m,m'}(t), \tag{12}$$

where $\rho_{m,m'}(t) = \sum_{L,M} \sqrt{\frac{2L+1}{2S+1}} C^{S,m'}_{S,m,L,M} \langle \hat{T}^{(S)}_{L,M} \rangle(t)$ are the matrix elements of the density matrix, the asterisk denotes the complex conjugate, and we have used the orthogonality property of the polarization operators [39], viz.

$$\mathrm{Tr}\{\hat{T}^{(S)}_{L_1,M_1} \hat{T}^{(S)}_{L_2,M_2}\} = (-1)^{M_1} \delta_{L_1,L_2} \delta_{M_1,-M_2}. \tag{13}$$

Thus the average value of any spin operator is simply the scalar $a^{(S)}_{L,M}(t)$ or linear combinations of it. For example, we have for the longitudinal component of the magnetization

$$\langle \hat{S}_Z \rangle(t) = \sqrt{S(S+1)(2S+1)/3} \langle \hat{T}^{(S)}_{1,0} \rangle(t) = \sqrt{S(S+1)(2S+1)/3} a_{1,0}(t). \tag{14}$$

The polarization operator expansion (9) also represents a direct analogue of the expansion of the classical distribution function $W(\vartheta, \varphi, t)$ of spin orientations in configuration space in terms of spherical harmonics (see, for example, [27])

$$W(\vartheta, \varphi, t) = \sum_{L=0}^{\infty} \sum_{M=-L}^{L} \langle Y_{L,M} \rangle(t) Y^*_{L,M}(\vartheta, \varphi), \tag{15}$$

where $\langle Y_{L,M} \rangle(t)$ are the averaged values of the spherical harmonics (statistical moments) and $Y^*_{L,M} = (-1)^M Y_{L,-M}$. This equivalence is clearly demonstrated using a bijective transformation introduced by Stratonovich [14] and further developed by others [15–24], namely

$$W^{(s)}_S(\vartheta, \varphi, t) = \mathrm{Tr}\{\hat{\rho}(t)\hat{w}_s\}, \tag{16}$$

where the transformation kernel $\hat{w}_s(\vartheta,\varphi)$ is defined as

$$\hat{w}_s(\vartheta,\varphi)=\sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}(C^{S,S}_{S,S,L,0})^{-s}Y^*_{L,M}\hat{T}^{(S)}_{L,M} \tag{17}$$

such that $\mathrm{Tr}\{\hat{w}_s\}=1$ and $[(2S+1)/4\pi]\int\hat{w}_s d\Omega=\hat{I}$ with $d\Omega=\sin\vartheta d\vartheta d\varphi$. Here the parameter s parametrizes quasiprobability functions of spins belonging to the SU(2) dynamical symmetry group [24]. The Stratonovich transformation (16) is the spin analogue of the well known Wigner transformation for translational motion [1, 25] (see, e.g., Refs. [14, 23, 24]). The phase space distribution function $W_S^{(s)}(\vartheta,\varphi,t)$ on the surface of the unit sphere for a spin system can now be obtained in explicit series form from the density matrix (9) and the kernel of the bijective transformation (17) because by definition [14]

$$W_S^{(s)}(\vartheta,\varphi,t)=\mathrm{Tr}\{\hat{\rho}(t)\hat{w}_s\}=\sqrt{\frac{4\pi}{2S+1}}\sum_{L=0}^{2S}\sum_{M=-L}^{L}(C^{S,S}_{S,S,L,0})^{-s}Y^*_{L,M}(\vartheta,\varphi)\langle\hat{T}^{(S)}_{L,M}\rangle(t) \tag{18}$$

by the orthogonality properties of the polarization operators. Furthermore, due to the orthogonality properties of the spherical harmonics [39], viz.,

$$\int Y_{L,M}(\Omega)Y^*_{L',M'}(\Omega)d\Omega=\delta_{L,L'}\delta_{M,M'},$$

Equation (18) can be presented as the finite series

$$\frac{2S+1}{4\pi}W_S^{(s)}(\vartheta,\varphi,t)=\sum_{L=0}^{2S}\sum_{M=-L}^{L}\langle Y_{L,M}\rangle^{(s)}(t)Y^*_{L,M}(\vartheta,\varphi), \tag{19}$$

where

$$\langle Y_{L,M}\rangle^{(s)}(t)=\frac{2S+1}{4\pi}\int Y_{L,M}(\Omega)W_S^{(s)}(\Omega,t)d\Omega=\sqrt{\frac{2S+1}{4\pi}}(C^{S,S}_{S,S,L,0})^{-s}\langle\hat{T}^{(S)}_{L,M}\rangle(t). \tag{20}$$

The distribution function $(2S+1)W_S^{(s)}(\vartheta,\varphi,t)/4\pi$ given by the finite series of (18) has a form similar to the expansion of the classical orientational distribution $W(\vartheta,\varphi,t)$, (15), and reduces to it in the classical limit, $S\to\infty$. We further remark that knowing the phase space distribution $W_S^{(s)}(\vartheta,\varphi,t)$, the density matrix $\hat{\rho}(t)$ can be reconstructed via the inverse Wigner-Stratonovich transformation [24]

$$\hat{\rho}(t)=\frac{2S+1}{4\pi}\int\hat{w}_s(\Omega)W_S^{(-s)}(\Omega,t)d\Omega. \tag{21}$$

In the above equations, the parameter values $s=0$ and $s=\pm1$ correspond to the Stratonovich [14] and Berezin [15] contravariant and covariant functions, respectively (the latter are directly related to the P- and Q-symbols which appear naturally in the coherent state representation; see Ref. [23] for a review). We now select $W_S^{(-1)}$ because at equilibrium this distribution alone satisfies the non-negative condition required of a true probability density function, viz., $W_S^{(-1)}\geq0$ and drop the superscript from now on. The quasiprobability densities $W_S^{(1)}$ and $W_S^{(0)}$ do not satisfy this condition (they may take on negative values in the present problem). We now determine the master equation in phase space using the inverse Wigner-Stratonovich transformation (21).

4 Master Equation in Phase-Space

By substituting the density matrix $\hat{\rho}$ in the form given by (21) into the reduced density matrix evolution equation (6), we have

$$\int \left(\hat{w} \frac{\partial}{\partial t} W_S - W_S \left\{ \frac{i}{\hbar\beta} (\sigma[\hat{S}_0^2, \hat{w}] + \xi[\hat{S}_0, \hat{w}]) + \mathrm{St}(\hat{w}) \right\} \right) d\Omega = 0. \tag{22}$$

As described in Appendix B, we then obtain [by algebraic transformations of (22)] the master equation for the phase space distribution $W_S(\vartheta, \varphi, t)$, viz.

$$\frac{\partial}{\partial t} W_S - \frac{\sigma}{\hbar\beta} \left(2S \cos\vartheta - \sin\vartheta \frac{\partial}{\partial\vartheta} + \frac{\xi}{\sigma} \right) \frac{\partial}{\partial\varphi} W_S = \mathrm{St}\{W_S\}, \tag{23}$$

where the collision kernel $\mathrm{St}\{W_S\}$ is

$$\begin{aligned} \mathrm{St}\{W_S\} = &\left\{ D_\parallel + D_\perp \frac{\cot\vartheta}{2\sin\vartheta} [(\bar{P}^{(S)} + 1)\cos\vartheta + \bar{P}^{(S)} - 1] \right\} \frac{\partial^2}{\partial^2\varphi} W_S \\ &+ \frac{D_\perp}{2\sin\vartheta} \frac{\partial}{\partial\vartheta} \left\{ \sin\vartheta [\bar{P}^{(S)} + 1 + (\bar{P}^{(S)} - 1)\cos\vartheta] \frac{\partial}{\partial\vartheta} \right. \\ &\left. + 2(\bar{P}^{(S)} - 1) S \sin^2\vartheta \right\} W_S. \end{aligned} \tag{24}$$

The differential operator $\bar{P}^{(S)}$ occurring in the collision kernel can be written as (see Appendix C)

$$\bar{P}^{(S)} = e^{\sigma+\xi} \sum_{l=0}^{2S} a_l \bar{P}_l^{(S)}, \tag{25}$$

where the operators $\bar{P}_l^{(S)}$ are defined by the upward recurrence equations

$$\bar{P}_l^{(S)} = A_{l-1} \bar{P}_{l-1}^{(S)} \bar{P}_1^{(S)} - A_{l-2} \bar{P}_{l-2}^{(S)} \tag{26}$$

which allows them to be calculated sequentially from $\bar{P}_0^{(S)} = (2S+1)^{-1/2}$ and

$$\bar{P}_1^{(S)} = \sqrt{3}[S(S+1)(2S+1)]^{-1/2} \left[(S+1)\cos\vartheta \pm \frac{1}{2\sin\vartheta} \frac{\partial}{\partial\vartheta} \pm i \frac{\partial}{\partial\varphi} \right].$$

The coefficients a_l, A_{l-1} and A_{l-2} are given in Appendix C by (C.2), (C.4), and (C.5), respectively. The left hand side of (23) is the quantum analogue of the Liouville equation for a spin. Furthermore, the collision operator given by (24) is a quantum analogue of the classical Fokker-Planck operator for rotational diffusion [27]. We reiterate that (23) follows from the equation of motion of the reduced density matrix (6), where the interactions between the spin and the heat bath are small enough to allow one to use the weak coupling limit and the correlation time characterizing the bath is so short that we can regard the stochastic process originating in the bath as Markovian. In longitudinal relaxation, the azimuthal angle dependence of W_S may be ignored so that the Liouville term vanishes in (23) and the corresponding evolution equation for $W_S(\vartheta, t)$ becomes

$$\frac{\partial W_S}{\partial t} = \frac{\partial}{\partial z} \left(D^{(2)} \frac{\partial}{\partial z} W_S - D^{(1)} W_S \right), \tag{27}$$

where $z = \cos\vartheta$, $D^{(1)} = D_\perp S(1-z^2)(1-\bar{P}^{(S)})$, and

$$D^{(2)} = D_\perp(1-z^2)[1-z+(1+z)\bar{P}^{(S)}]/2.$$

The master equation (27) is *formally* similar to the single spatial variable Fokker-Planck equation describing non-inertial rotational diffusion in an axially symmetric potential [27] and in the classical limit, (27) reduces to it as we shall demonstrate in Sect. 6.

5 Properties of the Master Equation (23)

We have already mentioned that the master equations (23) and (27) are *formally* similar to the corresponding classical Fokker-Planck equations describing non-inertial rotational diffusion of a magnetic dipole in an axially symmetric potential [27]. However, despite this similarity, (23) and (27) are in reality much more complicated than the Fokker-Planck equation for a classical uniaxial paramagnet because the differential operators $\bar{P}^{(S)}$ are now involved. The situation resembles the quantum translational Brownian motion of a particle in a potential $V(x)$, where derivatives of the Wigner function $W(x,p,t)$ of third and higher order appear in the underlying master equation [28–31]. However, for the *particular* case $\sigma = 0$ and $\xi \neq 0$, the higher order derivatives disappear and (23) takes on a much more simple form. This corresponds to a spin in a uniform field and has been treated in detail in Refs. [5, 6, 13]. We have from (23)

$$\begin{aligned}\frac{\partial}{\partial t}W_S - \frac{\xi}{\hbar\beta}\frac{\partial}{\partial\varphi}W_S = \frac{D_\perp(e^\xi-1)}{2\sin\vartheta}\Bigg\{&\cot\vartheta[\coth\xi\cos\vartheta+1]\frac{\partial^2}{\partial^2\varphi}W_S \\ &+\frac{\partial}{\partial\vartheta}\left[\sin\vartheta(\coth\xi+\cos\vartheta)\frac{\partial}{\partial\vartheta}W_S + 2S\sin^2\vartheta\, W_S\right]\Bigg\} \\ &+ D_\parallel\frac{\partial^2}{\partial^2\varphi}W_S. \qquad (28)\end{aligned}$$

Equation (28) coincides with that previously derived [5, 6] using the generalized coherent states formalism. In fact, it is the rotational analogue of the quantum translational harmonic oscillator treated using the Wigner function by Agarwal [40]. In this instance, the evolution equation for the Wigner distribution $W(x,p,t)$ in the phase space of positions and momenta is of the same mathematical form as the Fokker-Planck equation for the classical oscillator [40]

$$\frac{\partial W}{\partial t} + \frac{p}{m}\frac{\partial W}{\partial x} - m\omega_0^2 x\frac{\partial W}{\partial p} = \frac{\varsigma}{m}\frac{\partial}{\partial p}\left[pW + \langle p^2\rangle_{eq}\frac{\partial W}{\partial p}\right], \qquad (29)$$

where ς, m, and ω_0 are the “friction” coefficient, mass and oscillator frequency, respectively, $\langle p^2\rangle_{eq} = (m\hbar\omega_0/2)\coth(\beta\hbar\omega_0/2)$, except that the diffusion coefficient $D_{pp} = \varsigma\langle p^2\rangle_{eq}/m$ is altered in order to reflect the quantum mechanical behaviour. For longitudinal relaxation, where the distribution function W is independent of the azimuthal angle, the Liouville term in the evolution equation vanishes and (28) reduces to an equation very similar to that governing a classical spin in a uniform magnetic field [5, 6, 13]

$$\frac{\partial W_S}{\partial t} = D_\perp\frac{(e^\xi-1)}{2\sin\vartheta}\frac{\partial}{\partial\vartheta}\left\{(\sin\vartheta[\cos\vartheta+\coth\xi])\frac{\partial W_S}{\partial\vartheta} + 2S\sin^2\vartheta\, W_S\right\}. \qquad (30)$$

This simplification arises essentially because precession of a spin in a uniform field is effectively the rotational analogue of the translational harmonic oscillator.

In the absence of any potential whatsoever, i.e., when $\sigma = 0$ and $\xi = 0$, the operator $\bar{P}^{(S)}(0) = 1$ so that (23) becomes (setting $D_\parallel = D_\perp$)

$$\frac{\partial}{\partial t} W_S = D_\perp \left[\frac{1}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta \frac{\partial W_S}{\partial\vartheta} \right) + \frac{1}{\sin^2\vartheta} \frac{\partial^2 W_S}{\partial\varphi^2} \right]. \tag{31}$$

Thus the operator $\bar{P}^{(S)}$ can be considered as a *potential* operator differing from unity only if the potential is non zero. Equation (31) corresponds to the classical Fokker-Planck equation [27] for the orientational distribution function of the free magnetic dipole moments on a unit sphere. Hence just as the free quantum translational Brownian motion [1], the phase space distribution W of free spins obeys the classical Fokker-Planck equation. For large values of S ($S \gg 1$), since the terms involving derivatives in the operator equations [(23) et seq] now vanish, the operator $\bar{P}_l^{(S\gg1)} \to \sqrt{\frac{2l+1}{2S+1}} P_l$ so that the recurrence equation (26) simply becomes

$$(l+1) P_{l+1} - (2l+1)\cos\vartheta\, P_l + l P_{l-1} = 0. \tag{32}$$

This is one of the recurrence equations for the Legendre polynomials P_l, hence the operators can in the above limit be represented by these polynomials. Thus substituting the Legendre polynomials into (25) we must have

$$\bar{P}^{(S\to\infty)} = e^{\sigma+\xi} \sqrt{\frac{4\pi}{2S+1}} \sum_{l=0}^{2S} a_l Y_{l,0} = e^{\sigma+\xi} F^{(0)}(\vartheta, \varphi), \tag{33}$$

where the coefficients a_l are defined in (C.2) and

$$F^{(s)}(\vartheta, \varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{l=0}^{2S} (C^{S,S}_{S,S,l,0})^{-s} a_l Y_{l,0}$$

is the Weyl symbol of the operator $e^{2\sigma \hat{S}_0}$. For large S, $F^{(s)}(\vartheta, \varphi) \to e^{2\sigma S\cos\vartheta}$. Next by taking the limit $S \to \infty$, we have

$$\lim_{S\to\infty} S(e^{(\xi S + \sigma S + 2\sigma S^2 \cos\vartheta)/S} - 1) = \xi S + 2\sigma S^2 \cos\vartheta \quad \text{and} \quad \lim_{S\to\infty} e^{(\xi S + \sigma S + 2\sigma S^2\cos\vartheta)/S} = 1$$

Hence in the classical limit, $\beta \to 0$, $S \to \infty$, $\xi' = \xi S = \text{const}$, and $\sigma' = \sigma S^2 = \text{const}$, (23) reduces to (if $D_\perp = D_\parallel$)

$$\frac{\partial W}{\partial t} - \frac{\gamma}{\mu \sin\vartheta} \frac{\partial V}{\partial\vartheta} \frac{\partial W}{\partial\varphi} = D_\perp \Delta W + \frac{\beta D_\perp}{\sin\vartheta} \frac{\partial}{\partial\vartheta} \left(\sin\vartheta\, W \frac{\partial V}{\partial\vartheta} \right), \tag{34}$$

where $\beta V(\vartheta) = -\sigma' \cos^2\vartheta - \xi' \cos\vartheta$ and $\mu = \gamma\hbar S$ is the magnetic dipole moment. This equation corresponds to the classical Fokker-Planck equation for rotational diffusion of a magnetic dipole in the uniaxial potential [27].

6 Solutions of the Master Equation

The stationary solution of (23) and (27) is the equilibrium phase space distribution W_S^{eq} corresponding to the equilibrium spin density matrix $\hat{\rho}_{eq} = e^{-\beta \hat{H}_S} / \mathrm{Tr}\{e^{-\beta \hat{H}_S}\}$ defined by

(18) which yields

$$W_S^{eq}(\vartheta) = \mathrm{Tr}\{\hat{\rho}_{eq}\hat{w}(\vartheta)\}. \tag{35}$$

The distribution W_S^{eq} defined by (35) has been calculated in Ref. [41] and is given by

$$(S+1/2)W_S^{eq}(\vartheta) = \sum_{L=0}^{2S}(L+1/2)\langle P_L\rangle_{eq} P_L(\cos\vartheta), \tag{36}$$

where $\langle P_L\rangle_{eq} = (S+1/2)\int_0^\pi P_L(\cos\vartheta)W_S^{eq}(\vartheta)\sin\vartheta d\vartheta$ are the equilibrium values of the Legendre polynomials P_L given explicitly by

$$\langle P_L\rangle = Z_S^{-1} C_{S,S,L,0}^{S,S} \sum_{m=-S}^{S} C_{S,m,L,0}^{S,m} e^{\sigma m^2+\xi m}$$

and $Z_S = \mathrm{Tr}\{e^{-\beta\hat{H}_S}\} = \sum_{m=-S}^{S} e^{\sigma m^2+\xi m}$ is the partition function. For small S, e.g., for $S = 1/2, 1, 3/2$, etc. [41]

$$W_{1/2}^{eq}(\vartheta) = \frac{e^{\sigma/4}}{Z_{1/2}} f_\xi(\vartheta),$$

$$W_1^{eq}(\vartheta) = \frac{e^{\sigma}}{Z_1}[f_\xi^2(\vartheta) + \sin^2\vartheta(e^{-\sigma}-1)/2],$$

$$W_{3/2}^{eq}(\vartheta) = \frac{e^{9\sigma/4}}{Z_{3/2}}\left[f_\xi^3(\vartheta) + \frac{3}{4}(e^{-2\sigma}-1) f_\xi(\vartheta)\sin^2\vartheta\right],$$

etc., where $f_\xi(\vartheta) = \cosh(\xi/2) + \cos\vartheta\sinh(\xi/2)$. The distribution W_S^{eq} defined by (36) for $0 \le \vartheta \le \pi$ satisfies the non-negativity and normalization conditions,

$$W_S^{eq} \ge 0 \quad \text{and} \quad (S+1/2)\int W_S^{eq}(\vartheta)\sin\vartheta d\vartheta = 1$$

for all S as required of a true probability density function. In the classical limit, the distribution function W_S^{eq} becomes the Boltzmann distribution, i.e.,

$$(S+1/2)W_S^{eq}(\vartheta) \to Z_{cl}^{-1} e^{\xi'\cos\vartheta+\sigma'\cos^2\vartheta},$$

where Z_{cl} is the classical partition function. The quantum correction to the system with finite spin arises because the expansion of the quasi distribution function W_S^{eq} is a *finite* summation. In the classical case, corresponding to the limit $S \to \infty$, an infinite series in the Legendre polynomials is involved summing to the Boltzmann distribution $Z_{cl}^{-1} e^{\xi'\cos\vartheta+\sigma'\cos^2\vartheta}$. One can show analytically for small $S = 1/2, 1, 3/2$, etc. or numerically for arbitrary S that the collision kernel of (23) satisfies the condition

$$\mathrm{St}\{W_S^{eq}\} = 0,$$

i.e., the distribution W_S^{eq} defined by (36) is indeed a stationary solution of the master equations (23) and (27).

Referring to non-stationary solutions, the master equation (27) has been solved in Ref. [13] in the particular application to linear and nonlinear longitudinal relaxation of the spin in an external magnetic field, i.e., $\sigma = 0$, for *arbitrary* S (see also [10–12], where solutions are given for particular values of S). The methods of solution developed in Refs. [10–12] and [13] can also be used for $\sigma \neq 0$ (details elsewhere). Here we merely remark that a formal solution of equation (27) for arbitrary S may be given by expanding the distribution function $W_S(\vartheta, t)$ in a finite series of Legendre polynomials P_L just as for $\sigma = 0$ [13], viz.

$$W_S(\vartheta, t) = W_S^{eq}(\vartheta) + \sum_{L=0}^{2S} \frac{2L+1}{2S+1} P_L(\cos\vartheta) F_L^{(S)}(t), \tag{37}$$

where $F_L^{(S)}(t) = \langle P_L\rangle(t) - \langle P_L\rangle_{eq}$ are the desired statistical moments (relaxation functions) describing the spin dynamics. Substituting $W_S(\vartheta, t)$ in the form of (37) into (27) yields a system of $2S$ differential-recurrence equations for the relaxation functions $F_L(t)$, viz.,

$$\frac{d}{dt} F_L^{(S)}(t) = \sum_{L'} b_{L,L'}^{(S)} F_{L+L'}^{(S)}(t), \tag{38}$$

where $b_{L,L'}^{(S)}$ are coefficients of the system matrix. Equations (38) 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 [26, 27]. The results may be used to evaluate both the transient and ac (linear and nonlinear) responses of spins in magnetic fields. For example, knowing the linear response relaxation function $F_1^{(S)}(t)$, the longitudinal component of the magnetization $\langle \hat{M}_Z\rangle(t) \sim \langle \hat{S}_Z\rangle(t) - \langle \hat{S}_Z\rangle_0 = (S+1)F_1^{(S)}(t)$, the corresponding dynamic susceptibility

$$\chi_\parallel(\omega)/\chi_\parallel = 1 - i\omega[F_1^{(S)}(0)]^{-1} \int_0^\infty F_1^{(S)}(t) e^{-i\omega t} dt$$

($\chi_\parallel = \partial\langle \hat{S}_Z\rangle_0/\partial\xi$ is the static susceptibility) and integral relaxation time $\tau = [F_1^{(S)}(0)]^{-1} \int_0^\infty F_1^{(S)}(t)dt$ may be evaluated, just as the simple case $\sigma = 0$. The time τ characterizes the overall behavior of the magnetization $\langle \hat{M}_Z\rangle(t)$ and governs the low frequency behavior of $\chi_\parallel(\omega)$ [27], viz., $\chi_\parallel(\omega) = \chi_\parallel[1 - i\omega\tau + o(\omega)]$). Furthermore, since (27) has essentially the same mathematical form as the classical Fokker-Planck equation in the single coordinate ϑ, results already available for that equation (such as the explicit formula for τ [27]) may be directly carried over to the quantum case. For example, τ can be obtained in closed form using the equilibrium distribution $W_S^{eq}(\cos\vartheta)$ and diffusion coefficient $D^{(2)}$ alone because for dynamics obeying a single variable FPE

$$\tau = \frac{1}{\chi_\parallel} \int_{-1}^{1} \frac{\Psi(z)}{D^{(2)} W_S^{eq}(z)} \int_{-1}^{z} \frac{\partial}{\partial\xi} W_S^{eq}(x) dx dz, \tag{39}$$

where $\Psi(z) = (S+1/2)\int_{-1}^{z} [(S+1)y - \langle \hat{S}_Z\rangle_0] W_S^{eq}(y)dy$ and the variables of integration x, y, and z correspond to $\cos\vartheta$. The classical counterpart of this problem has been treated in Ref. [27, Chap. 8]; in the classical limit, the diffusion coefficient is $D^{(2)} = D_\perp(1 - z^2)$. An alternative calculation of τ for a uniaxial paramagnet has been given by Garanin [35] using the density matrix. In particular for $\sigma = 0$, although (39) and Garanin's expression [35] for τ have outwardly very different forms, the numerical results of both expressions coincide as shown in Ref. [13]. Thus an essential corollary between the phase space and the spin density matrix methods is established.

7 Concluding Remarks

We have shown how one may derive in the weak coupling limit a master equation for the evolution of the phase space quasi-probability distribution for a uniaxial spin system in contact with a heat bath at temperature T. It is supposed that the correlation time characterizing the bath is so short that the stochastic process originating in the bath is Markovian so that one may assume frequency independent damping. This is accomplished by first expressing the reduced density matrix master equation in terms of the inverse Wigner-Stratonovich transformation using (21). The various commutators involving the spin operators may then be evaluated by means of the orthogonality and recurrence properties of the polarisation operators and the corresponding spherical harmonics to yield their analogues in phase space. Thus one may express the master equation as a partial differential equation for the distribution function in the phase space of the polar angles. Despite the resemblance of the quantum diffusion equation (27) to the Fokker-Planck equation, for longitudinal relaxation of a spin in a uniaxial potential, equation (27) (governing the behaviour of the phase space distribution) is in reality much more complicated. The complications arise because the "drift" and "diffusion" coefficients $D^{(1)}$ and $D^{(2)}$ involve powers of differential operators up to $2S$ (S is the spin size considered), only simplifying for large spin values ($S \to \infty$) when the derivatives occurring in the operators may be ignored. For large spin values (of interest in studying the transition from magnetic cluster to single domain nanoparticle behaviour) the form of the differential operators suggests that perturbation in the inverse spin parameter $(2S+1)^{-1}$ (reminiscent of Wigner's original expansion of the translational Wigner distribution in powers of Planck's constant) may be useful in obtaining a tractable master equation for the distribution function [24]. Such an equation could then be reduced via suitable orthogonal expansions to differential recurrence relations which could be solved by continued fraction or matrix methods as commonly used in the solution of Fokker-Planck equations [26, 27].

We have illustrated the phase space representation of spin dynamics by treating an arbitrary spin in a uniform magnetic field of arbitrary strength directed along the easy axis of a uniaxial spin system. The main advantage of the phase space formalism is that only a master equation in configuration space akin to the Fokker-Planck equation is involved so that operators are unnecessary. Furthermore, the phase space representation suggests how powerful computation techniques developed for the Fokker-Planck equation may be extended to the quantum domain. Hence for spins (just as particles), the existing classical solution methods (matrix continued fractions, mean first passage time, etc. [26, 27]) also apply in the quantum case indeed suggesting new closed form quantum results via classical ones. The magnetization, dynamic susceptibility, characteristic relaxation times, etc., for the uniaxial system governed by the Hamiltonian given by (1), may now be evaluated (results will be published elsewhere). We remark that the spin dynamics of this uniaxial system have already been treated using the quantum Hubbard operator representation of the evolution equation for the spin density matrix [35–37] and indeed, as shown in Ref. [13], by considering spins in an external field alone the phase space and density matrix methods yield results in outwardly very different forms. Nevertheless, the numerical values from both methods for the same physical quantities (such as relaxation times and susceptibility) coincide, establishing an essential corollary between the phase space and the density matrix methods. Thus the phase space representation, because it is closely allied to the classical representation, besides being complementary to the operator representation, transparently illustrates how quantum distributions reduce to the classical ones. The analysis is carried out via the finite series in spherical harmonics embodied in the Wigner-Stratonovich map as we have illustrated for axially symmetric potentials. It may be extended in the appropriate limits to non-axially symmetric multi-well systems such as biaxial, cubic, etc. However, the difficulties (e.g., the operator form of the diffusion coefficients in the master equation) encountered in our discussion of axially symmetric potentials are indicative of the even greater difficulties faced when generalising the phase space representation to such non-axially symmetric multi-well potentials.

Finally we emphasize that the master equation (23) describes the relaxation of the phase space distribution $W_S(\vartheta,\varphi,t)$ to the equilibrium distribution W_S^{eq}, (36), corresponding to the canonical equilibrium density matrix $\hat{\rho}_{eq}$, (8). The canonical distribution describes the system in thermal equilibrium without coupling to the thermal bath. However, it is known from the theory of quantum open systems [42], that the equilibrium state may in general deviate from the canonical distribution $\hat{\rho}_{eq}$. Hence for open systems this distribution may describe the thermal equilibrium of the system in the weak coupling and high temperature limits only. A detailed discussion of this problem is given, e.g., by Geva et al. [43].

Acknowledgements This publication has proceeded with the financial support of Science Foundation Ireland (Project No. 05/RFP/PHY/0070).

Appendix A: Derivation of (7)

Equation (5) for the evolution of the reduced density matrix in the weak coupling limit can be rewritten as

$$\frac{\partial}{\partial t}\hat{\rho}(t)+\frac{i}{\hbar}[\hat{H}_S,\hat{\rho}(t)]=\mathrm{St}\{\hat{\rho}(t)\}, \tag{A.1}$$

where the collision kernel $\mathrm{St}\{\hat{\rho}(t)\}$ is given by

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

and we use the following form of the interaction operator $\hat{H}_{SB}$ [5, 6]

$$\hat{H}_{SB}=-\hbar\gamma\hat{\mathbf{h}}\cdot\hat{\mathbf{S}}=-\hbar\gamma(\hat{h}^0\hat{S}_0+\hat{h}^+\hat{S}_++\hat{h}^-\hat{S}_-) \tag{A.3}$$

with $\hat{h}^0=\hat{h}_z$ and $\hat{h}^\pm=(\hat{h}_x\mp i\hat{h}_y)/2$. We consider the operator $\hat{H}_{SB}$ in the form of (A.3) because it is a direct analogue of the classical Fokker-Planck equation for rotational diffusion of a magnetic dipole. Alternative forms of the operator $\hat{H}_{SB}$ are discussed, for example, in Ref. [36, 37]. On using the following properties of the correlation functions $\langle\hat{h}_i(t_1)\hat{h}_j(t_2)\rangle=Z_B^{-1}\mathrm{Tr}_B\{\hat{h}_i(t_1)\hat{h}_j(t_2)\hat{\rho}_B^{eq}\}$ (assuming axial symmetry about the Z-axis and $\langle\hat{\mathbf{h}}\rangle=0$)

$$\langle\hat{h}_x(t_1)\hat{h}_x(t_2)\rangle=\langle\hat{h}_y(t_1)\hat{h}_y(t_2)\rangle,\ldots,\langle\hat{h}^0(t_1)\hat{h}^\pm(t_2)\rangle=0,\quad\langle\hat{h}^\pm(t_1)\hat{h}^\pm(t_2)\rangle=0,$$

and the operator equalities

$$e^{\sigma\hat{S}_0^2+\xi\hat{S}_0}\hat{S}_\pm e^{-(\sigma\hat{S}_0^2+\xi\hat{S}_0)}=e^{\pm(2\sigma\hat{S}_0\mp\sigma\hat{I}+\xi\hat{I})}\hat{S}_\pm,\qquad \hat{S}_\pm e^{\mp(2\sigma\hat{S}_0\pm\sigma\hat{I}+\xi\hat{I})}=e^{\mp(2\sigma\hat{S}_0\mp\sigma\hat{I}+\xi\hat{I})}\hat{S}_\pm,$$

we have for the collision operator

$$\begin{aligned}\mathrm{St}\{\hat{\rho}(t)\}=\gamma^2\int_0^\infty&\{\langle\hat{h}^0(\tau)\hat{h}^0(0)\rangle[\hat{S}_0\hat{\rho}(t),\hat{S}_0]+\langle\hat{h}^0(0)\hat{h}^0(\tau)\rangle[\hat{S}_0,\hat{\rho}(t)\hat{S}_0]\\&+\langle\hat{h}^\pm(\tau)\hat{h}^\mp(0)\rangle[\hat{S}_\pm e^{i\tau\beta^{-1}(\pm2\sigma\hat{S}_0+\sigma\hat{I}\pm\xi\hat{I})}\hat{\rho}(t),\hat{S}_\mp]\\&+\langle\hat{h}^\mp(0)\hat{h}^\pm(\tau)[\hat{S}_\mp,e^{i\tau\beta^{-1}(\pm2\sigma\hat{S}_0-\sigma\hat{I}\pm\xi\hat{I})}\hat{\rho}(t)\hat{S}_\pm]\}d\tau,\end{aligned} \tag{A.4}$$

where $\hat{h}^j(\tau) = e^{i\hat{H}_B\tau/\hbar}\hat{h}^j(0)e^{-i\hat{H}_B\tau/\hbar}$ ($j = 0, \pm$). Here we have used the fact that the sets of operators $\{\hat{h}^j, e^{\pm i\hat{H}_B\tau/\hbar}, \hat{\rho}_B^{eq}\}$ and $\{\hat{S}_j, e^{\pm i\hat{H}_S\tau/\hbar}, \hat{\rho}\}$ are independent so that they may be considered separately. Next we introduce the Laplace transforms of the correlation functions, viz.

$$\tilde{C}_B^0(\omega) = \gamma^2 \int_0^\infty \langle \hat{h}^0(0)\hat{h}^0(\tau)\rangle e^{i\omega\tau} d\tau,$$

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

By noting that

$$\begin{aligned}
&e^{-\beta\hbar\omega} \int_0^\infty \langle \hat{h}^-(0)\hat{h}^+(\tau)\rangle e^{i\omega\tau} d\tau \\
&= Z_B^{-1} \int_0^\infty \sum_{k,l} e^{iE_k\tau/\hbar}[\hat{h}^+]_{k,l} e^{-iE_l\tau/\hbar}[\hat{h}^-]_{l,k} e^{-\beta E_k - \beta\hbar\omega} e^{i\omega\tau} d\tau \\
&= Z_B^{-1} \int_0^\infty \sum_{k,l} [\hat{h}^+]_{k,l} e^{-iE_l\tau/\hbar}[\hat{h}^-]_{l,k} e^{iE_k\tau/\hbar} e^{-\beta E_l} e^{i\omega\tau} d\tau \\
&= \left(\int_0^\infty \langle \hat{h}^-(\tau)\hat{h}^+(0)\rangle e^{-i\omega\tau} d\tau \right)^*,
\end{aligned}$$

($E_k - E_l + \hbar\omega = 0$), and assuming frequency independent damping, viz., $\tilde{C}_B^0(\omega) = \tilde{C}_B^{0*}(\omega) \to D_\parallel$ and $\tilde{C}_B(\omega) = \tilde{C}_B^*(\omega) \to D_\perp$, one obtains from (A.4) the reduced density matrix evolution equation (7).

Appendix B: Transformations of Operators Involved in (6) and (22)

Here we consider general relations facilitating the transformation of the density matrix evolution equation (6) into an equation for a quasiprobability distribution function $W_S(\vartheta, \varphi, t)$. We start with the commutation relations for the spin operators and their analogous differential operators in configuration space. We use the following commutation relation from the Liouville term in (6)

$$\begin{aligned}
[\hat{S}_0^2, \hat{w}] &= \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} (C_{S,S,L,0}^{S,S})^{-1} Y_{L,M}^* [\hat{S}_0^2, \hat{T}_{L,M}^{(S)}] \\
&= \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} (C_{S,S,L,0}^{S,S})^{-1} M Y_{L,M}^* \\
&\quad \times \left\{ \sqrt{\frac{[(L+1)^2 - M^2][(2S+1)^2 - (L+1)^2]}{(2L+3)(2L+1)}} \hat{T}_{L+1,M}^{(S)} \right. \\
&\quad \left. + \sqrt{\frac{(L^2 - M^2)[(2S+1)^2 - L^2]}{(2L-1)(2L+1)}} \hat{T}_{L-1,M}^{(S)} \right\}. \qquad \text{(B.1)}
\end{aligned}$$

By the replacement $L \pm 1 \to L$ in (B.1) and using the explicit expression for Clebsch-Gordan coefficients

$$C^{S,S}_{S,S,L,0} = (2S)!\sqrt{\frac{2S+1}{(2S-L)!(2S+L+1)!}}, \tag{B.2}$$

we have

$$\begin{aligned}
&\int W_S[\hat{S}_0^2, \hat{w}]d\Omega \\
&= \sqrt{\frac{4\pi}{2S+1}}\int W_S \sum_{L=0}^{2S} (C^{S,S}_{S,S,L,0})^{-1} \sum_{M=-L}^{L} \hat{T}^{(S)}_{L,M} M \\
&\times \left((2S-L+1)\sqrt{\frac{L^2-M^2}{4L^2-1}} Y^*_{L-1,M} + (2S+L+2)\sqrt{\frac{(L+1)^2-M^2}{(2L+3)(2L+1)}} Y^*_{L+1,M} \right) d\Omega.
\end{aligned} \tag{B.3}$$

In the last term of the right hand side of (B.3), we expand the summation as far as the indicated $L = 2S$. The terms containing the spherical harmonics $Y_{2S+1,M}$ vanish on averaging due to the orthogonality relations because the quasidistribution function W_S contains only spherical harmonics $Y_{L,M}$ up to order $L = 2S$. Noting that [39]

$$\cos\vartheta\, Y^*_{L,M} = \sqrt{\frac{(L+1)^2-M^2}{(2L+1)(2L+3)}} Y^*_{L+1,M} + \sqrt{\frac{L^2-M^2}{4L^2-1}} Y^*_{L-1,M},$$

$$\sin\vartheta \frac{\partial}{\partial\vartheta} Y^*_{L,M} = L\sqrt{\frac{(L+1)^2-M^2}{(2L+1)(2L+3)}} Y^*_{L+1,M} - (L+1)\sqrt{\frac{L^2-M^2}{4L^2-1}} Y^*_{L-1,M},$$

$$i\frac{\partial}{\partial\varphi} Y^*_{L,M} = M Y^*_{L,M},$$

we have

$$\int W_S[\hat{S}_0^2, \hat{w}]d\Omega = i\int W_S \left[\sin\vartheta \frac{\partial}{\partial\vartheta} + 2(S+1)\cos\vartheta\right] \frac{\partial}{\partial\varphi} \hat{w}\, d\Omega, \tag{B.4}$$

i.e., we have obtained that in the configuration representation the analogue of the commutator $[\hat{S}_0^2, \hat{w}]$ is the differential operator $i[\sin\vartheta\,\partial_\vartheta + 2(S+1)\cos\vartheta]\partial_\varphi \hat{w}$. Using integration by parts in (B.4), we obtain finally

$$\int W_S[\hat{S}_0^2, \hat{w}]d\Omega = i\int \hat{w} \left[\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\sin^2\vartheta - 2(S+1)\cos\vartheta\right] \frac{\partial}{\partial\varphi} W_S\, d\Omega. \tag{B.5}$$

The above derivation has been given in detail to illustrate the transformation of the master equation to the phase space representation. In the following, we now omit all these details and present only the final results. In particular, we have

$$[\hat{S}_0, \hat{w}] = i\frac{\partial}{\partial\varphi}\hat{w}, \tag{B.6}$$

$$[\hat{S}_0\hat{w},\hat{S}_0]+[\hat{S}_0,\hat{w}\hat{S}_0]=\frac{\partial^2}{\partial\varphi^2}\hat{w}. \tag{B.7}$$

Equations (B.5) and (B.6) allow one to obtain the Liouville (deterministic) part of the phase space master equation for W_S, viz.

$$\int W_S\{\sigma[\hat{S}_0^2,\hat{w}]+\xi[\hat{S}_0,\hat{w}]\}d\Omega=i\sigma\int\hat{w}\left(2S\cos\vartheta-\sin\vartheta\frac{\partial}{\partial\vartheta}+\frac{\xi}{\sigma}\right)\frac{\partial}{\partial\varphi}W_S d\Omega \tag{B.8}$$

and

$$\int W_S[\hat{S}_0\hat{w},\hat{S}_0]+[\hat{S}_0,\hat{w}\hat{S}_0]d\Omega=\int\hat{w}\frac{\partial^2}{\partial\varphi^2}W_S d\Omega. \tag{B.9}$$

Next consider the commutator $[\hat{S}_\pm\hat{w},\hat{S}_\mp]$ appearing in the collision kernel terms, we have

$$\int W_S[\hat{S}_\pm\hat{w},\hat{S}_\mp]d\Omega=\frac{1}{2}\int\hat{w}\left\{i\left(\sin\vartheta\frac{\partial}{\partial\vartheta}-2S\cos\vartheta\mp1\right)\frac{\partial}{\partial\varphi}\right.$$
$$\left.+\frac{1}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\left(\sin\vartheta(1\pm\cos\vartheta)\frac{\partial}{\partial\vartheta}\pm2S\sin^2\vartheta\right)+\cot\vartheta(\cos\vartheta\pm1)\frac{\partial^2}{\partial\varphi^2}\right]\right\}W_S d\Omega. \tag{B.10}$$

In the derivation of (B.10), the following properties of spherical harmonics have been used [39]

$$\frac{1}{\sin\vartheta}\frac{\partial}{\partial\vartheta}\left(\sin\vartheta\frac{\partial}{\partial\vartheta}Y_{L,M}^*\right)+\frac{1}{\sin^2\vartheta}\frac{\partial^2}{\partial^2\varphi}Y_{L,M}^*=-L(L+1)Y_{L,M}^*,$$
$$e^{\pm i\varphi}\left(\frac{\partial}{\partial\vartheta}\pm i\cot\vartheta\frac{\partial}{\partial\varphi}\right)Y_{L,M}^*=\mp\sqrt{L(L+1)-M(M\mp1)}Y_{L,M\mp1}^*,$$
$$\left(\frac{\partial^2}{\partial\vartheta^2}+\cot^2\vartheta\frac{\partial^2}{\partial\varphi^2}\pm i\frac{1}{\sin^2\vartheta}\frac{\partial}{\partial\varphi}\right)Y_{L,M}^*=-(L\mp M)(L\pm M+1)Y_{L,M}^*.$$

Noting that the commutator $[\hat{S}_\pm,\hat{w}\hat{S}_\mp]$ gives the complex conjugate differential operator to those corresponding to $[\hat{S}_\pm\hat{w},\hat{S}_\mp]$, we have

$$\int W_S([\hat{S}_\pm\hat{w},\hat{S}_\mp]+[\hat{S}_\pm,\hat{w}\hat{S}_\mp])d\Omega$$
$$=\frac{1}{2}\int\frac{\hat{w}}{\sin\vartheta}\left[\frac{\partial}{\partial\vartheta}\left(\sin\vartheta(1\pm\cos\vartheta)\frac{\partial}{\partial\vartheta}\pm2S\sin^2\vartheta\right)+\cot\vartheta(\cos\vartheta\pm1)\frac{\partial^2}{\partial\varphi^2}\right]W_S d\Omega. \tag{B.11}$$

By introducing the operator $P^{(S)}$ (which is defined explicitly in Appendix C) as

$$\int W_S[\hat{S}_+e^{\sigma(2\hat{S}_0+\hat{I})+\xi\hat{I}}\hat{w},\hat{S}_-]d\Omega=\int W_S[\hat{S}_+P^{(S)}\hat{w},\hat{S}_-]d\Omega, \tag{B.12}$$

using the transformation (B.10), we see that the commutator $[\hat{S}_\pm e^{\sigma(2\hat{S}_0+\hat{I})+\xi\hat{I}}\hat{w},\hat{S}_\mp]$ yields the same differential operator as that corresponding to the commutator $[\hat{S}_\pm\hat{w},\hat{S}_\mp]$

[see (B.10)] multiplied by $\bar{P}^{(S)}$; the latter is also defined in the Appendix C. Next we integrate (B.11) and (B.12) by parts. Substituting equations so obtained as well as (B.8) and (B.9) into (22), we obtain the phase space evolution equation (23).

Appendix C: Derivation of the Operator $\bar{P}^{(S)}$

The matrix exponent $e^{\sigma(2\hat{S}_0+\hat{I})+\xi\hat{I}}$ can be expanded in terms of the polarization operators as [39]

$$e^{\sigma(2\hat{S}_0+\hat{I})+\xi\hat{I}} = e^{\sigma+\xi}\sum_{l=0}^{2S} a_l \hat{T}_{l,0}^{(S)}, \tag{C.1}$$

where the scalar coefficients a_l can be found using the orthogonality property (13) and the explicit form of the matrix elements of the polarisation operator (10). These coefficients are

$$a_l = \mathrm{Tr}\{e^{2\sigma\hat{S}_0}\hat{T}_{l,0}^{(S)}\} = \sqrt{\frac{2l+1}{2S+1}}\sum_{m=-S}^{S} C_{S,m,l,0}^{S,m} e^{2\sigma m}. \tag{C.2}$$

In particular, we have the sequence

$$a_0 = \frac{\sinh[\sigma(2S+1)]}{\sqrt{2S+1}\sinh\sigma}, \qquad a_1 = \sqrt{\frac{3/4}{S(S+1)}}\frac{\partial}{\partial\sigma}a_0, \quad \text{etc.}$$

We consider the polarization operator $\hat{T}_{l,0}^{(S)}$ as an operator acting on the transformation function $\hat{w}$ and denote its analogues in phase space by $P_l^{(S)}$ and $\bar{P}_l^{(S)}$. The operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ are defined as

$$\int W_S \hat{T}_{l,0}^{(S)}\hat{w}\,d\Omega = \int W_S P_l^{(S)}\hat{w}\,d\Omega = \int \hat{w}\bar{P}_l^{(S)} W_S\,d\Omega. \tag{C.3}$$

The operator $\bar{P}_l^{(S)}$ can be obtained from the operator $P_l^{(S)}$ using integration by parts in the middle equation (C.3). The expansion (C.1) allows one to express both of the operators $P^{(S)}$ and $\bar{P}^{(S)}$ in terms of the operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ in the form of (25).

In order to find the explicit form of $P_l^{(S)}$ and $\bar{P}_l^{(S)}$, we recall that the product of the polarization operators $\hat{T}_{1,0}^{(S)}\hat{T}_{l,0}^{(S)}$ [39] is

$$\hat{T}_{1,0}^{(S)}\hat{T}_{l,0}^{(S)} = \frac{1}{2}\sqrt{\frac{3}{S(S+1)(2S+1)}} \times\left(l\sqrt{\frac{(2S+1)^2-l^2}{4l^2-1}}\hat{T}_{l-1,0}^{(S)} + (l+1)\sqrt{\frac{(2S-l)(2S+l+2)}{(2l+1)(2l+3)}}\hat{T}_{l+1,0}^{(S)}\right).$$

This may be presented as the upward recurrence equation

$$\hat{T}_{l,0}^{(S)} = A_{l-1}\hat{T}_{1,0}^{(S)}\hat{T}_{l-1,0}^{(S)} - A_{l-2}\hat{T}_{l-2,0}^{(S)},$$

where the coefficients A_{l-1} and A_{l-2} are given by

$$A_{l-1} = \frac{2}{l}\sqrt{\frac{S(S+1)(2S+1)(4l^2-1)}{3[(2S+1)^2-l^2]}}, \tag{C.4}$$

$$A_{l-2} = \frac{l-1}{l}\sqrt{\frac{(2l+1)[(2S+1)^2-(l-1)^2]}{(2l-3)[(2S+1)^2-l^2]}}. \tag{C.5}$$

The operators $P_l^{(S)}$ and $\bar{P}_l^{(S)}$ satisfy a similar recurrence equation

$$\begin{pmatrix} \hat{P}_l^{(S)} \\ \bar{P}_l^{(S)} \end{pmatrix} = A_{l-1}\begin{pmatrix} \hat{P}_{l-1}^{(S)}\hat{P}_1^{(S)} \\ \bar{P}_{l-1}^{(S)}\bar{P}_1^{(S)} \end{pmatrix} - A_{l-2}\begin{pmatrix} \hat{P}_{l-2}^{(S)} \\ \bar{P}_{l-2}^{(S)} \end{pmatrix}$$

with $P_0^{(S)} = \bar{P}_0^{(S)} = (2S+1)^{-1/2}$ and

$$\begin{pmatrix} P_1^{(S)} \\ \bar{P}_1^{(S)} \end{pmatrix} = \sqrt{\frac{3}{S(S+1)(2S+1)}}\left[(S+1)\cos\vartheta \pm \frac{1}{2}\begin{pmatrix} \sin\vartheta \\ 1/\sin\vartheta \end{pmatrix}\frac{\partial}{\partial\vartheta} \pm i\frac{\partial}{\partial\varphi}\right]. \tag{C.6}$$

For longitudinal relaxation, the φ dependence may be ignored, so that the operator $\frac{\partial}{\partial\varphi}$ in the right hand side of (C.6) must be omitted. Thus the phase space differential operators $P^{(S)}$ and $\bar{P}^{(S)}$ can be finally presented as

$$\begin{pmatrix} P^{(S)} \\ \bar{P}^{(S)} \end{pmatrix} = e^{\sigma+\xi}\sum_{l=0}^{2S} a_l \begin{pmatrix} P_l^{(S)} \\ \bar{P}_l^{(S)} \end{pmatrix}. \tag{C.7}$$

References

1. de Groot, S.R., Suttorp, L.G.: Foundations of Electrodynamics. North-Holland, Amsterdam (1972), Chaps. VI and VII
2. Schleich, W.P.: Quantum Optics in Phase Space. Wiley-VCH, Berlin (2001)
3. Haken, H.: Laser Theory. Springer, Berlin (1984)
4. Narducci, L.M., Bowden, C.M., Bluemel, V., Carrazana, G.P.: Phase-space description of the thermal relaxation of a $(2J+1)$-level system. Phys. Rev. A **11**(1), 280–287 (1975)
5. Takahashi, Y., Shibata, F.: Spin coherent state representation in non-equilibrium statistical mechanics. J. Phys. Soc. Jpn. **38**(3), 656–668 (1975)
6. Takahashi, Y., Shibata, F.: Generalized phase space method in spin systems—spin coherent state representation. J. Stat. Phys. **14**(1), 49–65 (1976)
7. Perelomov, A.M.: Generalized Coherent States and Their Applications. Springer, Berlin (1986)
8. Nashitsume, N., Shibata, F., Shingu, M.: Quantal master equation valid for any time scale. J. Stat. Phys. **17**(4), 155–169 (1977)
9. Shibata, F., Takahashi, Y., Nashitsume, N.: A generalized stochastic Liouville equation. Non-Markovian versus memoryless master equations. J. Stat. Phys. **17**(4), 171–187 (1977)
10. Shibata, F.: Theory of nonlinear spin relaxation. J. Phys. Soc. Jpn. **49**(1), 15–24 (1980)
11. Shibata, F., Asou, M.: Theory of nonlinear spin relaxation. II. J. Phys. Soc. Jpn. **49**(4), 1234–1241 (1980)
12. Shibata, F., Ushiyama, C.: Rigorous solution to nonlinear spin relaxation process. J. Phys. Soc. Jpn. **62**(2), 381–384 (1993)
13. Kalmykov, Y.P., Coffey, W.T., Titov, S.V.: Phase-space formulation of the nonlinear longitudinal relaxation of the magnetization in quantum spin systems. Phys. Rev. E **76**(5), 051104 (2007)
14. Stratonovich, R.L.: On distributions in representation space. Zh. Eksp. Teor. Fiz. **31**(6), 1012–1020 (1956) [Sov. Phys. JETP **4**(6), 891–898 (1957)]
15. Berezin, F.A.: General concept of quantization. Commun. Math. Phys. **40**(2), 153–174 (1975)

16. Scully, M.O., Wodkiewicz, K.: Spin quasi-distribution functions. Found. Phys. **24**(1), 85–107 (1994)
17. Radcliffe, J.M.: Some properties of coherent spin states. J. Phys. A: Math. Gen. **4**(3), 313–323 (1971)
18. Arecchi, F.T., Courtens, E., Gilmore, R., Thomas, H.: Atomic coherent states in quantum optics. Phys. Rev. A **6**(6), 2211–2237 (1972)
19. Agarwal, G.S.: Relaxation between atomic coherent-state representation, state multipoles, and generalized phase-space distributions. Phys. Rev. A **24**(6), 2889–2896 (1981)
20. Agarwal, G.S.: State reconstruction for a collection of two-level systems. Phys. Rev. A **57**(1), 671–673 (1998)
21. Dowling, J.P., Agarwal, G.S., Schleich, W.P.: Wigner distribution of a general angular-momentum state: Applications to a collection of two-level atoms. Phys. Rev. A **49**(5), 4101–4109 (1994)
22. Brif, C., Mann, A.: Phase-space formulation of quantum mechanics and quantum-state reconstruction for physical systems with Lie-group symmetries. Phys. Rev. A **59**(2), 971–987 (1999)
23. Várilly, J.C., Gracia-Bondía, J.M.: The Moyal representation for spins. Ann. Phys. (NY) **190**(1), 107–148 (1989)
24. Klimov, A.B.: Exact evolution equations for SU(2) quasidistribution functions. J. Math. Phys. **43**(5), 2202–2213 (2002)
25. Wigner, E.P.: On the quantum correction for thermodynamic equilibrium. Phys. Rev. **40**, 749–759 (1932)
26. Risken, H.: The Fokker-Planck Equation, 2nd edn. Springer, Berlin (1989)
27. Coffey, W.T., Kalmykov, Y.P., Waldron, J.T.: The Langevin Equation, 2nd edn. World Scientific, Singapore (2004)
28. García-Palacios, J.L.: Solving quantum master equations in phase space by continued-fraction methods. Europhys. Lett. **65**(6), 735–741 (2004)
29. García-Palacios, J.L., Zueco, D.: The Caldeira–Leggett quantum master equation in Wigner phase space: continued-fraction solution and application to Brownian motion in periodic potentials. J. Phys. A: Math. Gen. **37**, 10735–10770 (2004)
30. Coffey, W.T., Kalmykov, Yu.P., Titov, S.V., Mulligan, B.P.: Semiclassical master equation in Wigner's phase space applied to Brownian motion in a periodic potential. Phys. Rev. E **75**(4), 041117 (2007)
31. Coffey, W.T., Kalmykov, Yu.P., Titov, S.V.: Solution of the master equation for Wigner's quasiprobability distribution in phase space for the Brownian motion of a particle in a double well potential. J. Chem. Phys. **127**(7), 074502 (2007)
32. Slichter, C.P.: Principles of Magnetic Resonance. Springer, Berlin (1990) and references therein
33. Blum, K.: Density Matrix: Theory and Applications. Plenum, New York (1996)
34. Zubarev, D., Morozov, V., Röpke, G.: Statistical Mechanics of Nonequilibrium Processes, vol. 1. Akademie, Berlin (2001)
35. Garanin, D.A.: Quantum thermoactivation of nanoscale magnets. Phys. Rev. E **55**(3), 2569–2572 (1997)
36. García-Palacios, J.L., Zueco, D.: Solving spin quantum master equations with matrix continued-fraction methods: application to superparamagnets. J. Phys. A: Math. Gen. **39**, 13243–13284 (2006)
37. Zueco, D., García-Palacios, J.L.: Longitudinal relaxation and thermoactivation of quantum superparamagnets. Phys. Rev. B **73**, 104448 (2006)
38. Wangsness, R.K., Bloch, F.: The dynamical theory of nuclear induction. Phys. Rev. **89**, 728–739 (1953)
39. Varshalovich, D.A., Moskalev, A.N., Khersonskii, V.K.: Quantum Theory of Angular Momentum. World Scientific, Singapore (1998)
40. Agarwal, G.S.: Brownian motion of a quantum oscillator. Phys. Rev. A **4**(2), 739–747 (1971)
41. Kalmykov, Y.P., Coffey, W.T., Titov, S.V.: Phase-space equilibrium distribution function for spins. J. Phys. A: Math. Theor. **41**(10), 105302 (2008)
42. Weiss, U.: Quantum Dissipative Systems, 2nd edn. World Scientific, Singapore (1999)
43. Geva, E., Rosenman, E., Tannor, D.: On the second-order corrections to the quantum canonical equilibrium density matrix. J. Chem. Phys. **113**(4), 1380–1390 (2000)