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Phase space equilibrium distribution function for spins

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Abstract

The equilibrium quasiprobability density function $W(\vartheta, \varphi)$ of spin orientations in a representation (phase) space of the polar and azimuthal angles (ϑ, φ) (analogous to the Wigner distribution for translational motion of a particle) is given by a finite series of spherical harmonics in the spin number and their associated statistical moments so allowing one to calculate $W(\vartheta, \varphi)$ for an *arbitrary* spin system in the equilibrium state described by the canonical distribution $\hat{\rho} = \mathrm{e}^{-\beta \hat{H}_S}/\mathrm{Tr}(\mathrm{e}^{-\beta \hat{H}_S})$. The system with Hamiltonian $\hat{H}_S = -\gamma\hbar\mathbf{H}\cdot\hat{\mathbf{S}} - B\hat{S}_Z^2$ is treated as a particular example (γ is the gyromagnetic ratio, $\hbar$ is Planck's constant, $\mathbf{H}$ represents an external magnetic field and B represents an internal field parameter). For a uniaxial system with $\hat{H}_S = -\gamma\hbar H\hat{S}_Z - B\hat{S}_Z^2$, the solution may be given in the closed form.

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(Some figures in this article are in colour only in the electronic version)

The phase space representation of the density matrix extensively used in quantum optics (see, e.g., [1–2]) when applied to spin systems [3, 4] allows one to describe quantum spin problems in terms of a *quasiprobability density function* $W(\vartheta, \varphi)$ of spin orientations in a phase (here configuration) or representation space (ϑ, φ); ϑ and φ are the polar and azimuthal angles, respectively, constituting the canonical variables. The advantage of such a mapping of the density matrix onto a c-number quasiprobability density function is that one may determine how $W(\vartheta, \varphi)$ evolves as a function of the spin. This is of particular interest in the study of molecular nanomagnets [5]. Moreover, the distribution function reduces to the Boltzmann distribution of orientations in the classical limit. The quasiprobability density $W(\vartheta, \varphi)$ was originally introduced by Stratonovich [6] as part of a general discussion of c-number quasiprobability distributions for quantum systems in representation space based on the symmetry properties of the underlying group. Examples are the Heisenberg–Weyl group for particles and the $SU(2)$ group for rotations. Phase space representations for spin operators have been discussed in detail in [7–14]. The formulation of quantum mechanics [13] in terms of phase space functions instead of Hilbert space states and operators allows quantum mechanical expectation values to be evaluated in terms of phase space integrals just as classical averages. Thus, it is eminently suited to the calculation of quantum corrections to the classical expectation values. This is accomplished [13] via the Stratonovich–Weyl correspondence stemming in Stratonovich's formulation, from a linear bijective mapping between operators on the Hilbert space and functions in a representation space which is classically meaningful (e.g., classical phase space or the space of orientations [14]). Phase space methods which were first introduced into quantum mechanics by Wigner [15] contain only those features common to both classical and quantum mechanics and in general they reformulate quantum mechanics as a statistical theory on the representation space, a procedure known as the Moyal quantization [16].

By the way of background, we remark that Wigner [15] originally arrived at his quasiprobability density $W(x, p)$ for translational motion of a particle in the phase space (x, p), which is the quasiprobability representation of the density operator simply by requiring that, the marginal distributions of $W(x, p)$ should yield the correct quantum mechanical probability densities for the position x and momentum p of the particle with Hamiltonian $\hat{H} = \hat{p}^2/2m + V(\hat{x})$ in phase space. He thus established a one-to-one correspondence [17] between the quantum state $|\psi\rangle$ in the particle Hilbert space and a real phase space function $W(x, p)$ which is also called the Wigner transform. The Moyal quantization is so called because Moyal [16] discovered by introducing a characteristic function operator $\hat{M}(\tau, \theta) = \exp[\mathrm{i}(\tau\hat{p} + \theta\hat{x})]$ of the position and momentum that the Weyl correspondence rule between c-numbers and operators can be inverted via the Wigner transform from an operator on the Hilbert space to a function in the phase space. Stratonovich [6] on the other hand in attempting to generalize the Moyal quantization to spins governed by the $SU(2)$ rotation group (the quasiprobability density function $W(\vartheta, \varphi)$ is entirely analogous to $W(x, p)$ for the Heisenberg–Weyl group except that certain differences arise because of the angular momentum commutation relations [6]) discovered a linear bijective mapping [cf equation (1)–(3) of [6] between operators on the Hilbert space and functions in the representation space. This mapping [14] satisfies a number of physically intuitive properties, covariance and tracing being the two most important, and essentially replaces Moyal's characteristic function operator. Thus, representation space distributions can be determined via this bijective map from the general definition of a representation distribution using the symmetry properties of the underlying group.

Up to the present, however, phase space methods for spins have been mainly applied in quantum optics and very little attention has been paid to other spin systems. For example, explicit equations for the equilibrium distribution $W(\vartheta, \varphi)$ have been given only for a spin $\mathbf{S}$ in a uniform magnetic field $\mathbf{H}$ [3]. Here by applying the phase space formalism [6–14], we present a *general* approach to the calculation of the phase space distributions $W(\vartheta, \varphi)$ for spin systems with equilibrium states described by the canonical density matrix $\hat{\rho}$ given by

$$\hat{\rho} = \mathrm{e}^{-\beta\hat{H}_S}/Z_S, \tag{1}$$

where $Z_S = \mathrm{Tr}\{\mathrm{e}^{-\beta\hat{H}_S}\}$ is the partition function for an arbitrary Hamiltonian $\hat{H}_S$. In view of the importance of the uniaxial anisotropy potential in applications to magnetism, quantum optics, etc (see, e.g., [18–22]), we shall illustrate this approach by evaluating $W(\vartheta, \varphi)$ for a uniaxial paramagnet of an arbitrary spin value S in an external *constant* field $\mathbf{H}$ so that the Hamiltonian is

$$\beta\hat{H}_S = -\xi(\gamma_X\hat{S}_X + \gamma_Y\hat{S}_Y + \gamma_Z\hat{S}_Z) - \sigma\hat{S}_Z^2, \tag{2}$$

where $\gamma_X, \gamma_Y, \gamma_Z$ are the direction cosines of the field $\mathbf{H}$, σ and ξ are the dimensionless internal and external field parameters, respectively and $\beta = 1/(kT)$ is the inverse thermal energy.

The phase space distribution function $W^{(s)}(\vartheta,\varphi)$ on the surface of the unit sphere for a spin system given by Stratonovich [6] (see also [14]) is given by

$$W^{(s)}(\vartheta,\varphi) = \mathrm{Tr}\{\hat{\rho}\hat{w}_s(\vartheta,\varphi)\}, \tag{3}$$

where s parameterizes quasiprobability functions of spins belonging to the $SU(2)$ dynamical symmetry group such as considered here, $\hat{w}_s(\vartheta,\varphi)$ is the Wigner–Stratonovich operator (or kernel) defined as [14]

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

such that [cf equations (3) and (6) of [6] $\mathrm{Tr}\{\hat{w}_s(\vartheta,\varphi)\} = 1$,

$$\frac{2S+1}{4\pi}\int_{\theta,\varphi} W^{(s)}\,\mathrm{d}\Omega = 1, \qquad \text{and} \qquad \frac{2S+1}{4\pi}\int_{\theta,\varphi}\hat{w}_s\,\mathrm{d}\Omega = \hat{I}$$

where $\mathrm{d}\Omega = \sin\vartheta\,\mathrm{d}\vartheta\,\mathrm{d}\varphi$, the asterisk denotes the complex conjugate and $\hat{I}$ is the identity matrix. Here, $Y_{L,M}(\vartheta,\varphi)$ are the spherical harmonics [23], $\hat{T}^{(S)}_{L,M}$ are the irreducible tensor (polarization) operators with matrix elements given by [23]

$$\left[\hat{T}^{(S)}_{L,M}\right]_{m',m} = \sqrt{\frac{2L+1}{2S+1}}C^{S,m'}_{S,m,L,M}, \tag{5}$$

and $C^{S,S}_{S,S,L,0}$ and $C^{S,m'}_{S,m,L,M}$ are the Clebsch–Gordan coefficients [23]. The function $W^{(-s)}(\vartheta,\varphi)$ now allows us to calculate the *average* value $\langle\hat{A}\rangle = \mathrm{Tr}\{\hat{\rho}\hat{A}\}$ of an arbitrary spin operator $\hat{A}$ because the $W^{(-s)}(\vartheta,\varphi)$ provides the overlap relation [6]

$$\langle\hat{A}\rangle = \frac{2S+1}{4\pi}\int_{\theta,\varphi} A_s(\vartheta,\varphi)W^{(-s)}(\vartheta,\varphi)\,\mathrm{d}\Omega, \tag{6}$$

where $A_s(\vartheta,\varphi) = \mathrm{Tr}\{\hat{A}\hat{w}_s(\vartheta,\varphi)\}$ is the Weyl symbol of the operator $\hat{A}$ (see, e.g., [16]). The parameter values $s = 0$ and $s = \pm 1$ correspond to the Stratonovich [6] and Berezin [9] 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 [11] for a review). Here we consider $W^{(-1)}(\vartheta,\varphi)$ only; thus we omit everywhere the superscript -1 in $W^{(-1)}(\vartheta,\varphi)$ ($W^{(1)}(\vartheta,\varphi)$ and $W^{(0)}(\vartheta,\varphi)$ can be treated in like manner). We have chosen $W^{(-1)}(\vartheta,\varphi)$ because this distribution alone satisfies the nonnegativivity condition required of a true probability density function, namely, $W^{(-1)}(\vartheta,\varphi) \geqslant 0$. The quasiprobability densities $W^{(1)}(\vartheta,\varphi)$ and $W^{(0)}(\vartheta,\varphi)$ violate this condition because they may take on negative values in the present problem.

In order to proceed, we first recall that the spin density matrix $\hat{\rho}$ is represented by a $(2S+1)\times(2S+1)$ square matrix [23]. The Hermitian ($\hat{\rho} = \hat{\rho}^{\dagger}$) and normalized ($\mathrm{Tr}\,\hat{\rho} = 1$) density matrix $\hat{\rho}$ may be expanded as a sum of the polarization operators $\hat{T}^{(S)}_{L,M}$, namely [23],

$$\hat{\rho} = \sum_{L=0}^{2S}\sum_{M=-L}^{L}(-1)^M a_{L,-M}\hat{T}^{(S)}_{L,M}, \tag{7}$$

where the expansion coefficients $a_{L,M}$ (representing expectation values of $\hat{T}^{(S)}_{L,M}$ in a state described by the density matrix $\hat{\rho}$) are given by [23]

$$a_{L,M} = \left\langle\hat{T}^{(S)}_{L,M}\right\rangle = \mathrm{Tr}\left\{\hat{\rho}\hat{T}^{(S)}_{L,M}\right\}. \tag{8}$$

Substituting equations (7) and (4) into equation (3) and noting that $\mathrm{Tr}\left\{\hat{T}^{(S)}_{L',M'}\hat{T}^{(S)}_{L,M}\right\} = (-1)^{M'}\delta_{L',L}\delta_{M',-M}$, we have after some algebra the phase space distribution in Fourier series form which emphasizes the relationship with the representation of the associated classical Boltzmann distribution in terms of spherical harmonics, namely,

$$W(\vartheta,\varphi) = \sqrt{\frac{4\pi}{2S+1}} \sum_{L=0}^{2S} \sum_{M=-L}^{L} C_{S,S,L,0}^{S,S} a_{L,M} Y_{L,M}^{*}(\vartheta,\varphi). \tag{9}$$

Equation (9) is a general result valid for an *arbitrary* spin system with equilibrium states described by the canonical density matrix $\hat{\rho}$ given by equation (1). The phase space distribution from equation (9) is similar to that introduced by Agarwal *et al* [10, 24, 25], who explicitly gave the distribution for atomic angular momentum Dicke states, coherent states and squeezed states corresponding to a collection of two-level atoms. We shall show below how in the present explicit series form equation (9) allows one to evaluate equilibrium distributions for spins.

As an example of the application of equation (9), we calculate the Wigner function of a spin system with the Hamiltonian $\hat{H}_S$ given by equation (2). Noting that the spin operators $\hat{S}_X$, $\hat{S}_Y$and $\hat{S}_Z$ can be expressed in terms of the polarization operators $\hat{T}_{1,M}^{(S)}$ as [23] $\hat{S}_X = a\big[\hat{T}_{1,-1}^{(S)} - \hat{T}_{1,1}^{(S)}\big]$, $\hat{S}_Y = \mathrm{i}a\big[\hat{T}_{1,-1}^{(S)} + \hat{T}_{1,1}^{(S)}\big]$ and $\hat{S}_Z = \sqrt{2}a\hat{T}_{1,0}^{(S)}$, where $a = \sqrt{S(S+1)(2S+1)/6}$, and using equation (5), we can (i) present the Hamiltonian $\hat{H}_S$ from equation (2) in the explicit matrix form, next (ii) evaluate numerically the density matrix $\hat{\rho}$ from equation (1), hence (iii) calculate the coefficients $a_{L,M}$ from equation (8); having thus estimated $a_{L,M}$, we can (iv) calculate the distribution $W(\vartheta,\varphi)$ from equation (9) for any particular S. We remark that for the problem in question the matrix elements of $\hat{H}_S$ can also be given in a closed form without using the operators $\hat{T}_{1,M}^{(S)}$, namely

$$[\hat{H}_S]_{m',m} = A^{(-)}\delta_{m,m'+1} + A^{(+)}\delta_{m,m'-1} - (\sigma m^2 + \gamma_Z \xi m)\delta_{m,m'},$$

where $A^{(\pm)} = -(1/2)\xi(\gamma_X \pm \mathrm{i}\gamma_Y)\sqrt{(S\pm m)(S\mp m+1)}$. Results of the calculation of $\beta V(\vartheta,\varphi) = \mathrm{const} - \ln W(\vartheta,\varphi)$ ($V(\vartheta,\varphi)$ has the meaning of an 'effective' free energy potential) are shown in figure 1 for various values of S and $\sigma' = \sigma S^2 = 5$, $h = \xi S/2\sigma = 0.2$, $\gamma_Z = 1/2$, $\gamma_Y = 0$ and $\gamma_X = \sqrt{3}/2$ (i.e., the field $\mathbf{H}$ is in the XZ plane and directed at an angle $\pi/3$ to the Z-axis). The effective potential $V(\vartheta,\varphi)$ has two nonequivalent minima (the second minimum at $\vartheta = \pi$ is masked in these plots) and one saddle point in the plane $\varphi = 0$; the potential characteristics (such as the shape and barrier heights) strongly depend on S. In the classical limit ($S\to\infty$, $\xi S = \mathrm{const} = \xi'$, $\sigma S^2 = \mathrm{const} = \sigma'$), the function $V(\vartheta,\varphi)$ tends to the normalized classical free energy $V_{cl}(\vartheta,\varphi)$ given by

$$\beta V_{cl}(\vartheta,\varphi) = \mathrm{const} - \sigma'\{\cos^2\vartheta + 2h[(\gamma_X\cos\varphi + \gamma_Y\sin\varphi)\sin\vartheta + \gamma_Z\cos\vartheta]\}, \tag{10}$$

which is also shown in figure 1 for comparison.

As an example of how the general equation (9) can be considerably simplified when the matrix elements $\rho_{m,m'}$ of the equilibrium spin density matrix $\hat{\rho} = \mathrm{e}^{-\beta\hat{H}_S}/Z_S$ are given explicitly, we obtain the Wigner function of a system with Hamiltonian given by equation (2) for the particular uniaxial case, $\gamma_X = 0$, $\gamma_Y = 0$ and $\gamma_Z = 1$, namely, $\beta\hat{H}_S = -\xi\hat{S}_Z - \sigma\hat{S}_Z^2$, which is of importance in magnetic applications [18–20]. Here the density matrix $\hat{\rho}$ is diagonal with matrix elements $\rho_{m,m'}$ given by [18, 20]

$$\rho_{m,m'} = \delta_{m,m'}\,\mathrm{e}^{\sigma m^2+\xi m}/Z_S, \tag{11}$$

where $Z_S = \sum_{m=-S}^{S} \mathrm{e}^{\sigma m^2+\xi m}$. The $\rho_{m,m'}$ can now be used to evaluate the coefficients $a_{L,M}$ as [23]

$$a_{L,M} = \sqrt{\frac{2L+1}{2S+1}} \sum_{m,m'=-S}^{S} C_{S,m,L,M}^{S,m'} \rho_{m,m'}. \tag{12}$$

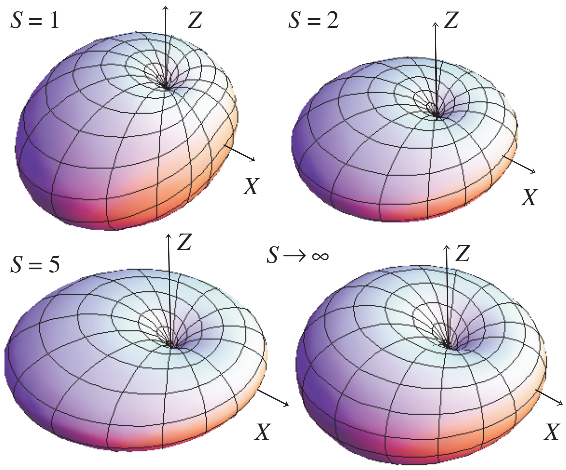

Figure 1. 3D plot of $\beta V(\vartheta, \varphi)$ for various values of $S = 1$, 2, 5 and $S \to \infty$ (classical limit; equation (10)).

Due to the symmetry about the Z-axis, the phase space distribution function W is independent of the azimuthal angle φ so that equation (9) can be simplified to (noting equation (12) and that $Y_{L,0}(\vartheta, \varphi) = \sqrt{(2L+1)/4\pi}\, P_L(\cos\vartheta)$)

$$(S+1/2)\, W(\vartheta) = \sum_{L=0}^{2S} (L+1/2)\, \langle P_L \rangle\, P_L(\cos\vartheta). \tag{13}$$

Here $\langle P_L \rangle = (S+1/2)\int_0^{\pi} P_L(\cos\vartheta) W(\vartheta) \sin\vartheta\, \mathrm{d}\vartheta$ are the equilibrium values of the Legendre polynomials P_L given explicitly by

$$\langle P_L \rangle = Z_S^{-1} C_{S,S,L,0}^{S,S} \sum_{m=-S}^{S} C_{S,m,L,0}^{S,m}\, \mathrm{e}^{\sigma m^2 + \xi m}. \tag{14}$$

We remark that the statistical moment $\langle P_1 \rangle$ yields the average longitudinal component of the spin

$$\langle \hat{S}_Z \rangle = (S+1)\langle P_1 \rangle = (S+1)\langle \cos\vartheta \rangle = Z_S^{-1} \sum_{m=-S}^{S} m\, \mathrm{e}^{\sigma m^2 + \xi m}$$

which is in complete agreement with the known result for the equilibrium magnetization for any S [20]. Here we have noted that the Weyl symbol for the operator $\hat{S}_Z$ is $S_Z(\vartheta, \varphi) = \mathrm{Tr}\{\hat{S}_Z \hat{w}_1(\vartheta, \varphi)\} = (S+1)\cos\vartheta$ [14]. By using explicit equations for the Legendre polynomials $P_L(\cos\vartheta)$ [26] in equation (13), we have closed form results, e.g., for $S = 1/2, 1, 3/2, 2, 5/2$, etc.

$$W(\vartheta) = \mathrm{e}^{\sigma/4} f_\xi(\vartheta)/Z_{1/2},$$

$$W(\vartheta) = \mathrm{e}^{\sigma}\left[f_\xi^2(\vartheta) + (1/2)(\mathrm{e}^{-\sigma} - 1)\sin^2\vartheta\right]\big/ Z_1,$$

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

$$W(\vartheta) = \frac{\mathrm{e}^{4\sigma}}{Z_2}\left[f_\xi^4(\vartheta) + (\mathrm{e}^{-3\sigma} - 1) f_\xi^2(\vartheta)\sin^2\vartheta + \frac{1}{8}(3\mathrm{e}^{-4\sigma} - 4\mathrm{e}^{-3\sigma} + 1)\sin^4\vartheta\right],$$

$$W(\vartheta) = \frac{e^{25\sigma/4}}{Z_{5/2}}\left[f_\xi^5(\vartheta) + \frac{5}{4}(e^{-4\sigma}-1)f_\xi^3(\vartheta)\sin^2\vartheta + \frac{5}{16}(2e^{-6\sigma}-3e^{-4\sigma}+1)f_\xi(\vartheta)\sin^4\vartheta\right],$$

where $f_\xi(\vartheta) = \cosh(\xi/2) + \sinh(\xi/2)\cos\vartheta$. For *arbitrary* S, the series in $f_\xi^{2(S-m)}(\vartheta)\sin^{2m}\vartheta$ for the distribution $W(\vartheta)$ can be written as

$$W(\vartheta) = Z_S^{-1} e^{S^2\sigma}\sum_{n=0}^{[S]} b_n f_\xi^{2(S-n)}(\vartheta)\sin^{2n}\vartheta, \tag{15}$$

where $[S]$ means the whole part of S and the leading coefficients b_n are

$$b_0 = 1, \qquad b_1 = (S/2)[e^{-(2S-1)\sigma} - 1],$$
$$b_2 = (S/16)[(2S-1)e^{-4(S-1)\sigma} - 4(S-1)e^{-(2S-1)\sigma} + 2S - 3]\text{ etc.}$$

For $\sigma = 0$, i.e., for a spin in a uniform external magnetic field, when the Hamiltonian becomes $\beta\hat{H}_S = -\xi\hat{S}_Z$, equation (13) reduces to the known results [3] (in our notation)

$$W(\vartheta) = f_\xi^{2S}(\vartheta)/Z_S, \tag{16}$$

where $Z_S = \sinh[(S+1/2)\xi]/\sinh(\xi/2)$. The distribution (16) is a quantum analogue of the Boltzmann distribution for classical magnetic dipoles μ precessing in the magnetic field $\mathbf{H}$ (the precession frequency ω_0 being $\omega_0 = \gamma H$). It is also the spin analogue of the Wigner function $W(x, p)$ for a *quantum Brownian oscillator* of mass m and natural frequency ω_0, namely [27]

$$W(x,p) = Z'^{-1} e^{-\frac{m}{\hbar\omega_0}\tanh\frac{\beta\hbar\omega_0}{2}(\omega_0^2x^2+p^2/m^2)},$$

where $Z' = \pi\hbar\coth(\beta\hbar\omega_0/2)$.

The distribution $W(\vartheta)$ is shown in figure 2 as a function of the polar angle ϑ. The maxima of $W(\vartheta)$ occur at $\vartheta = 0$ and $\vartheta = \pi$ and are given by

$$W(0) = Z_S^{-1} e^{S\xi+S^2\sigma} \qquad \text{and} \qquad W(\pi) = Z_S^{-1} e^{-S\xi+S^2\sigma},$$

respectively, meaning classically that the spins are concentrated at the bottom of the wells, where the minima of the potential energy occur. In the classical limit, namely,

$$S\to\infty, \qquad \sigma\to 0, \qquad \xi\to 0, \qquad \sigma S^2 = \text{const} = \sigma', \qquad \xi S = \text{const} = \xi',$$

$W(\vartheta)$ from equation (13) tends to the Boltzmann distribution, i.e.,

$$(S+1/2)W(\vartheta) \to Z_{cl}^{-1} e^{\xi'\cos\vartheta+\sigma'\cos^2\vartheta}, \tag{17}$$

where $Z_{\rm cl} = \int_0^\pi e^{\xi'\cos\vartheta+\sigma'\cos^2\vartheta}\sin\vartheta\,d\vartheta$ is the classical partition function. As one can see in figure 2(*a*), the deviations of the quantum distribution $(S+1/2)\,W(\vartheta)$ from the classical Boltzmann distribution equation (17) are pronounced only for small spin numbers $S < 10$. As S increases, the distribution $(S+1/2)\,W(\vartheta)$ becomes very close to the Boltzmann distribution equation (17) (e.g, for $S = 20$, the differences between the two distributions do not exceed 10 per cent; see the curve 5 in figure 2(*a*)). Due to the biasing effect of the external field, the maxima are unequal in height. In the low temperature limit, where the dynamics of the spin in the vicinity of the maxima $\vartheta = 0$ and $\vartheta = \pi$ comprise a precession in the effective magnetic field $H^{\pm} = (\beta\gamma\hbar)^{-1}[\pm\xi + (2S-1)\sigma]$, $W(\vartheta)$ can be approximated as

$$W(\vartheta) \approx Z_S^{-1} e^{-\sigma S(S-1)} f_{\xi\pm(2S-1)\sigma}^{2S}(\vartheta), \qquad \begin{pmatrix}\vartheta \leqslant 1\\ \pi-\vartheta \leqslant 1\end{pmatrix}. \tag{18}$$

As seen in figure 2(*b*), the 'oscillator' function *f* from equation (16) describes with a very high degree of accuracy the behavior of $W(\vartheta)$ near $\vartheta = 0$ and $\vartheta = \pi$.

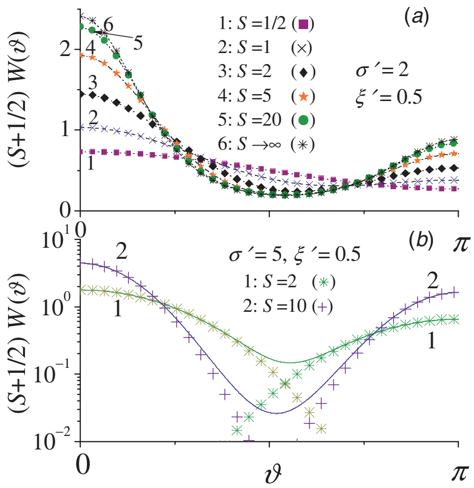

Figure 2. (*a*) $(S+1/2)\,W(\vartheta)$versus ϑ for $\sigma'=2$, $\xi'=0.5$ and various values of S including the classical limit, $S\to\infty$, equation (17). (*b*) The distribution $(S+1/2)\,W(\vartheta)$ (solid lines) for $\sigma'=5$, $\xi'=0.5$, and $S=2$ and 10. Crosses ($\times$) and stars ($*$): equation (18).

We have shown in this paper how the phase space method may be used to construct equilibrium distribution functions in the configuration space of polar angles (ϑ,φ) (which are now the canonical variables) for spin systems in the equilibrium state described by the canonical distribution $\hat{\rho}=\mathrm{e}^{-\beta\hat{H}_S}/Z_S$. The system with Hamiltonian $\hat{H}_S=-\gamma\hbar\mathbf{H}\cdot\hat{\mathbf{S}}-B\hat{S}_Z^2$ has been treated as a particular example. However, other spin systems including those with nonaxially symmetric Hamiltonians such as $\hat{H}_S=-A\hat{S}_X^2-B\hat{S}_Z^2$ (a biaxial system), $\hat{H}_S=-C\left(\hat{S}_X^4+\hat{S}_Y^4+\hat{S}_Z^4\right)$ (a cubic system), etc can be treated in like manner. The Wigner function may be represented using the Wigner–Stratonovich map as a Fourier series just as the corresponding classical orientational distribution and transparently reduces to it in the classical limit. Moreover, relevant quantum mechanical averages (such as the magnetization) may be calculated in a manner analogous to the corresponding classical averages using the Weyl symbol of the appropriate quantum operator (see equation (6)). The Wigner functions can now be applied to important magnetic problems such as the estimation of the spin dependence of the switching fields and hysteresis curves, which require only a knowledge of equilibrium distributions. This fact is important particularly from an experimental point of view as the transition between magnetic molecular cluster and single domain ferromagnetic nanoparticle behavior is essentially demarcated via the hysteresis loops and the corresponding switching fields [28]. Furthermore, these functions are important, in the interpretation of quantum tunneling phenomena in ferromagnetic nanoparticles and molecular magnets (see, e.g., [5, 28]) and also in the crossover region between reversal of the magnetization of these particles by thermal agitation and reversal by macroscopic quantum tunneling which is of current topical interest [18, 20, 28]. For instance, by analogy with the original classical calculation of Néel [29], the simplest description of quantum effects in the magnetization reversal time of a nanoparticle would be provided by the inverse escape rate from the wells of the magnetocrystalline and external field potential as calculated by quantum transition state theory (TST) [30, 31]. TST ignores the disturbance to the equilibrium distribution in the wells created by the loss of the magnetization due to escape over the barrier and so involves the equilibrium distribution only as that is assumed to prevail everywhere. However, the equilibrium quantum distribution is also essential in the inclusion of *nonequilibrium* effects in the quantum escape rate. Now a quantum master equation describing the time evolution of the quasiprobability density in the representation space is required in order to generalize the classical escape rate calculations pioneered by Kramers [32] for point particles and by Brown [33, 34] for single domain ferromagnetic particles using the Fokker–Planck equation. The diffusion coefficients in that equation are calculated using Einstein's imposition [35] of the Maxwell–Boltzmann distribution as the equilibrium solution. Just as the Fokker–Planck equation, by postulating [35, 36] in the quantum master equation, a Kramers–Moyal-like expansion truncated at the second term for the collision term the diffusion coefficients may be calculated by requiring that the equilibrium distribution in the representation space renders the collision term zero. In the present context this has been illustrated for the particular case of a spin in a uniform field in [37] indicating clearly how all the solution methods developed for the classical Fokker–Planck equation carry over seamlessly to the quantum case just as the corresponding solutions for particles [35, 36]. Yet another advantage of the phase space representation is that via TST as corrected for spin size effects (which is readily apparent from that representation), it is possible to predict the temperature dependence of the switching fields and corresponding hysteresis loops within the limitations imposed by TST. This is likely to be of interest in experiments seeking evidence for macroscopic quantum tunneling where the temperature dependence of the loops is crucial as the loops are used [28] to demarcate tunneling behavior from thermal agitation behavior.

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