PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

A Two Rotor Model with spin for magnetic Nanoparticles

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We argue that a kind of magnetic nanoparticles might exist characterized by the locking of the constituent spins with the density profile of the macrospin. We represent such nanoparticles by two interacting rigid rotors one of which has a large spin attached to the body, namely by a Two Rotor Model with spin. By this model we can describe in a unified way the cases of nanoparticles free and stuck in an elastic or rigid matrix. We evaluate the magnetic susceptibility for the latter case and under some realistic assumptions we get results in closed form. A crossover between thermal and purely quantum hopping occurs at a temperature much larger than that at which tunneling becomes important. Agreement with some experimental data is remarkable.

PACS numbers: 75.75+a, 75.75.Jn, 61.46.Df

1. *Introduction.* We consider single domain nanoparticles that can schematically be represented as a uniform magnetic lattice, the macrospin, rotating in a nonmagnetic lattice. While it seems natural to associate a rigid rotor with the nonmagnetic lattice [1], the macrospin is generally represented as a pure spin. We think however that in some cases, possibly several cases, also the macrospin should carry a moment of inertia because the constituting spins will always to some extent drag the orbits. One extreme example is given by structures in which the constituting spins belong to electrons that have such a strong spin-orbit coupling that they are rigidly locked to their orbits. Another example occurs when the macrospin has an electrically charged profile, so that its magnetic moment gets a contribution from the orbital motion. Actually the role of the moment of inertia in the dynamics of a finite system of particles was already considered long ago for ions in crystals [2], and recently for the Scissors Modes of electrons in metal clusters [3] and quantum dots [4] and of ions in crystals [5,6]. Concerning nanoparticles, an inertial parameter was often explicitly introduced in the treatment of tunneling, but only recently, as far as we know, it appeared in the theory of the classical regime [7].

We restrict our attention to nanoparticles that can be represented as two rigid rotors one of which carries a large spin. For such nanoparticles we adopt a model obtained by a modification of the Two Rotor Model designed long ago [8] to describe deformed atomic nuclei, in which case the two rotors are the proton and neutron bodies as shown in Fig.1. The Two Rotor Model predicts collective excitations called Scissors Modes characterized by a strong magnetic dipole moment (generated by the rotation of the proton electric charge around the bisector of the proton and neutron axes), whose coupling with the electromagnetic field provides their signature. Scissors Modes have been observed for the first time [9] in a rare earth nucleus, ^{156}Gd, and then in all deformed atomic nuclei. By analogy similar collective excitations were predicted [10] and observed [11] in Bose-Einstein condensates and predicted (but not yet experimentally searched or found) in several other systems, including metal clusters [12], quantum dots [4], Fermi [13] condensates and crystals [5,6]. In all these cases one of the scissors blades must be identified with a structure at rest and the other one with a moving cloud of particles.

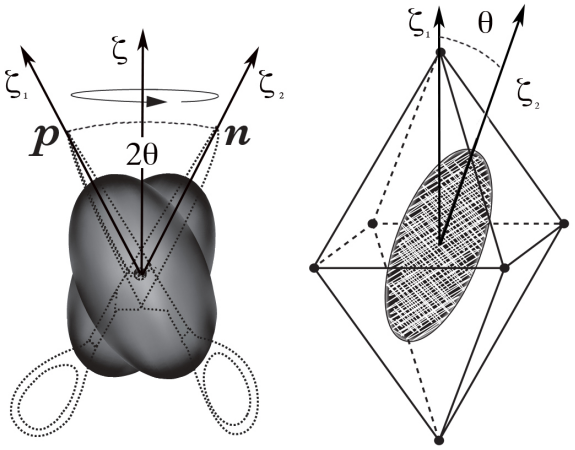

FIG. 1: Two Rotor Model: On the left the proton (p) and neutron (n) rotors precess around the bisector ζ of their axes ζ_1, ζ_2. On the right the charge profile of an ion in an octahedral cell is rigidly locked to its spin, indicated by an arrow. In both cases the lowest excited states are called Scissors Modes. The right figure represents also a nanoparticle if we identify the octahedron with the nonmagnetic lattice of easy axis ζ_1 and the ion with the macrospin pointing in the direction ζ_2.

Before proceeding, we want to stress an analogy between a nanoparticle stuck in a rigid matrix and a magnetic ion in a crystal cell. Such an analogy is closer when the electrons of the ions that carry the magnetism have such a strong spin-orbit coupling that their charge density profile is rigidly locked with the spin, as shown in Fig.1. In a recent work [6] we adapted the Two Rotor Model to such a system representing the magnetic ion

with spin-orbit locking as a rigid rotor with spin. In the present paper we will exploit this analogy.

In order to put our model into perspective let us examine the characteristic features of the magnetic susceptibility of single domain nanoparticles. We consider a system in which such objects are well separated so that they can be regarded as noninteracting with one another. Moreover we assume the nonmagnetic lattice to be axially symmetric and to have the easy axis of magnetization along the symmetry axis. We can refer to Fig.1 if we imagine the octahedron replaced by a lattice with so many sites to acquire approximately an axial symmetry. Then we assume that the magnetic lattice is made of a huge number of spins rigidly locked together in such a way that its body has also axial symmetry and can be represented by a rigid rotor with spin as in Fig.1. The nonmagnetic lattice provides a double well potential for the macrospin that at room temperature will undergo thermal fluctuations so that in the absence of an external magnetic field the neat magnetization of the nanoparticle will vanish. Such behavior is essentially classical, and can be described as the precession of a magnetic moment under the effect of different forces by classical thermodynamics or the Landau-Lifshitz-Gilbert equation [14]. One should expect, however, that at sufficiently low temperature the macrospin will be blocked along one of the two orientations of the easy axis giving a neat magnetic moment to the nanoparticle. Instead it was first observed by Weil [15] that down to 1K, at least one quarter of the macrospins remained unblocked in Nickel nanoparticles. It was then suggested by Bean and Livingstone [16] that even at such low temperature the macrospin might still fluctuate not because of thermic motion but because of quantum tunneling, and a crossover (appearing as an inflection in the susceptibility) should occur between classical and quantum behaviour at some critical temperature T_c. This interpretation was adopted to explain anomalous relaxation phenomena discovered at low temperature in other magnetic systems [17] and further investigated in Refs. [18–21]. Much of the work on this subject is reviewed in Ref. [22].

As a further example for nanoparticles we quote the results of Ref.[23], in which a change of curvature can be seen at a temperature of the order of 1K. There are examples for several other systems. Below certain temperatures the a.c. susceptibility of one dimensional coordination polymers [24] exhibits signals of a second peak. This feature, interpreted as a crossover between relaxation processes, is common to many other similar systems with a Single-Molecule Magnet behavior. They are TM or RE clusters that individually exhibit the properties of a magnet below a critical temperature called the blocking temperature (the maximum temperature at which the magnetization does not flip during the time of measurement). Because of their size, much smaller or comparable to the smallest magnetic particles, they exhibit quantum tunneling of magnetization and quantum phase interference [25].

So the appearance of quantum effects at low temperature is a rather general phenomenon in several magnetic systems. Some of the systems investigated do not consist of magnetic particles with a unique barrier, but rather of particles having a distribution of energy barriers [22], others have a single domain structure, but even for this latter simpler case we are not aware of any simple model that can reproduce at the same time the classical and the quantum behavior characterizing the crossover.

Our model predicts a crossover between a classical and a quantum regime, in which thermal hopping of the macrospin is replaced by quantum hopping. Quantum tunneling, instead, appears at a much smaller temperature.

The application of the Two Rotor Model with spin is different in the cases in which the non magnetic lattice is stuck in a rigid matrix, or it is stuck in an elastic matrix or it is altogether free. In the latter cases one must take into account effects due to angular momentum conservation, because rotation of the macrospin entails rotation of the nonmagnetic lattice [20]. But all these situations can be described in a unified framework. Having in mind future applications, we will present this model in its full generality, even though detailed calculations have been performed only for nanoparticles stuck in a rigid matrix.

2. *The Two Rotor Model with spin.* The general form of the Two Rotor Model Hamiltonian [8] is

$$H = \frac{1}{2\mathcal{I}_1}\vec{L}_1^2 + \frac{1}{2\mathcal{I}_2}\vec{L}_2^2 + V \qquad (1)$$

where $\vec{L}_1, \vec{L}_2$, $\mathcal{I}_1, \mathcal{I}_2$ are the angular momenta and moments of inertia of the nonmagnetic lattice and macrospin respectively, and V the sum of the potential interaction between them plus an external potential. We denote by $\hat{\zeta}_1, \hat{\zeta}_2$ the symmetry axes of the nonmagnetic lattice and the macrospin, and assume the easy axis of magnetization along $\hat{\zeta}_1$ and the spin along $\hat{\zeta}_2$. We write the wave functions of the macrospin as functions of the polar angles, $\psi = \psi(\theta_2, \phi_2)$, with the understanding that the spin has the direction of $\vec{\zeta}_2$. We can invert the direction of the spin by performing an inversion of $\vec{\zeta}_2$. We can construct even and odd wave functions with respect to spin inversion I_s: $I_s\psi_\sigma(\theta,\varphi) = \sigma\psi_\sigma(\theta,\varphi)\,,\ \sigma = \pm 1$. The interaction between the two rotors will depend only on the angle 2θ between $\hat{\zeta}_1, \hat{\zeta}_2$, $\cos(2\theta) = \hat{\zeta}_1 \cdot \hat{\zeta}_2$. The independent variables are $\hat{\zeta}_1, \hat{\zeta}_2$. They can be replaced by variables that describe the system of the rotors as a whole plus the variable θ. To this end we define a frame of axes

$$\hat{\xi} = \frac{\hat{\zeta}_2 \times \hat{\zeta}_1}{2\sin\theta},\ \hat{\eta} = \frac{\hat{\zeta}_2 - \hat{\zeta}_1}{2\sin\theta},\ \hat{\zeta} = \frac{\hat{\zeta}_2 + \hat{\zeta}_1}{2\cos\theta} \qquad (2)$$

and denote by α, β, γ its Euler angles. The correspondence $\{\hat{\zeta}_1, \hat{\zeta}_2\} = \{\alpha, \beta, \gamma, \theta\}$ is one-to-one and regular for $0 < \theta < \frac{\pi}{2}$. The variables $\{\hat{\zeta}_1, \hat{\zeta}_2\} = \{\alpha, \beta, \gamma, \theta\}$ are not sufficient to describe the configurations of the classical system, but they describe uniquely the quantized system

owing to the constraints $\vec{L}_1 \cdot \hat{\zeta}_1 = 0,\ \vec{L}_2 \cdot \hat{\zeta}_2 = 0$ necessary for rigid bodies with axial symmetry. These constraints are automatically satisfied if we take the wave functions to depend on $\hat{\zeta}_1, \hat{\zeta}_2$ only. Because of these constraints the component of the total angular momentum of the macrospin along $\vec{\zeta}_2$ is constant and equal to the spin.

We can now transform the Hamiltonian in the new variables. We define the operators

$$\vec{L} = \vec{L}_1 + \vec{L}_2,\ \ \vec{\mathcal{L}} = \vec{L}_1 - \vec{L}_2\,. \tag{3}$$

$\vec{L}$ is the total orbital angular momentum acting on the Euler angles α, β, γ, while $\vec{\mathcal{L}}$ is not an angular momentum, and has the representation [8]

$$\mathcal{L}_\xi = i\frac{\partial}{\partial\theta},\ \ \mathcal{L}_\eta = -\cot\theta L_\zeta,\ \ \mathcal{L}_\zeta = -\tan\theta L_\eta\,. \tag{4}$$

The transformed Hamiltonian is the sum of the rotational kinetic energy of the two rotors system as a whole plus an intrinsic energy

$$H = \frac{\vec{\mathcal{L}}^2}{2\mathcal{I}} + H_I \tag{5}$$

where $\mathcal{I} = \mathcal{I}_1\mathcal{I}_2/(\mathcal{I}_1 + \mathcal{I}_2)$. The intrinsic energy reads

$$H_I = \frac{1}{2\mathcal{I}}\left[\cot^2\theta\mathcal{L}_\zeta^2 + \tan\theta^2\mathcal{L}_\eta^2 - \frac{\partial^2}{\partial\theta^2} - 2\cot(2\theta)\frac{\partial}{\partial\theta}\right] + \frac{\mathcal{I}_1 - \mathcal{I}_2}{4\mathcal{I}_1\mathcal{I}_2}\left[-\tan\theta\mathcal{L}_\zeta\mathcal{L}_\eta - \cot\theta\mathcal{L}_\eta\mathcal{L}_\zeta + i\mathcal{L}_\zeta\frac{\partial}{\partial\theta}\right] + V\,. \tag{6}$$

This Hamiltonian was studied in detail [8] for $\mathcal{I}_1 \sim \mathcal{I}_2$ and small θ, as appropriate to atomic nuclei.

In such a general formulation of the Two Rotor Model the motion of the two rotors is decomposed into their relative motion in the intrinsic frame and the motion of the system as a whole. Because it is customary and convenient to denote by θ the angle between a moving axis and the third axis of the frame of reference, that in this case is the bisector of the angle between $\hat{\zeta}_1, \hat{\zeta}_2$, the latter angle was denoted by 2θ, see Fig.1.

In the present paper we study the magnetic susceptibility of a nanoparticle stuck in a rigid matrix. In such a case the macrospin moves in the frame of the nonmagnetic lattice, whose third axis is $\hat{\zeta}_1$, and then we denote the angle between $\hat{\zeta}_1$ and $\hat{\zeta}_2$ by θ, see Fig.1(b). Therefore

$$H = \frac{\hbar^2}{2\mathcal{I}}\left(-\frac{\partial^2}{\partial\theta^2} - \cot\theta\frac{\partial}{\partial\theta} - \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right) + V \tag{7}$$

where $\mathcal{I}$ the moment of inertia of the macrospin with respect to the ξ- and η-axes. In the presence of an ac magnetic field $\vec{H}_{ac}$ of angular frequency ω we assume the potential

$$V = \frac{1}{2}C\sin^2\theta - \vec{\mu}\cdot\vec{H}_{ac}\cos(\omega t)\,, \tag{8}$$

where C is a restoring force constant due to the electric and magnetic interactions of the macrospin with the nonmagnetic lattice and $\vec{\mu}$ is the intrinsic magnetic moment of the macrospin. Here this magnetic moment is a phenomenological parameter, that in microscopic models is assumed to come mostly from the spins of a huge number $\sim 10^3 - 10^5$ of electrons locked together, with a possible orbital contribution. But since in our model this magnetic moment is oriented along the macrospin symmetry axis, it comes from the constituting spins only, the orbital contribution vanishing because of the quantum condition $\vec{L}_2 \cdot \vec{\zeta}_2 = 0$. The components of the magnetic moment of the macrospin along the axes ξ_2, η_2 are instead nonvanishing in general, and contribute to the magnetic susceptibility, but we assume for simplicity that the macrospin does not have an electrically charged profile, so that there is no orbital contribution at all to the magnetic moment.

In the present preliminary investigation we consider one noninteracting nanoparticle in an ac magnetic field.

3. *Reactive susceptibility and spectrum of the Two Rotors Model.* We report only the study of the reactive susceptibility whose general expression for one nanoparticle is

$$\chi' = \frac{1}{Z}\sum_{\alpha\alpha'} <\alpha|\cos\theta|\alpha'><\alpha'|\vec{\mu}\cdot\vec{H}_{ac}|\alpha> \Phi_{\alpha,\alpha'} \tag{9}$$

where

$$\Phi_{\alpha,\alpha'} = (\nu_\alpha - \nu_{\alpha'})\,\frac{E_{\alpha'} - E_\alpha - \hbar\omega}{(E_{\alpha'} - E_\alpha - \hbar\omega)^2 + \Gamma^2}\,. \tag{10}$$

In the last equation E_α are the eigenvalues of the two rotor Hamiltonian in the absence of the ac magnetic field, $\nu_\alpha = \exp(-E_\alpha/k_BT)\,,\ \ Z = \sum_\alpha \nu_\alpha$, k_B being the Boltzman constant. Γ is the amplitude of spontaneous transitions between the levels α, α' assumed to be level independent. We neglected the elastic term that contributes only for $\omega = 0$.

The representation of nanoparticles by rigid rotors, however, cannot be valid at all temperatures. There will be a *maximum temperature* T_M, beyond which the nanoparticle will change shape or will be altogether demagnetized. This will provide an effective cut off to the spectrum, that we divide into three regions.

Region I, $E_\alpha \ll C$, harmonic oscillator modes. We assume that

$$\theta_0^2 = \hbar/\sqrt{\mathcal{I}C} \ll 1. \tag{11}$$

The wave functions of the lowest lying states are then localized at small values of θ so that for such states the potential can be approximated by a double well. For $0 < \theta < \pi/2$ the Hamiltonian (7) becomes

$$H = H_0 - \vec{\mu}\cdot\vec{H}_{ac}\cos(\omega t) \tag{12}$$

where

$$H_0 = \frac{\hbar^2}{2\mathcal{I}}\left(-\frac{\partial^2}{\partial\,\theta^2} - \frac{1}{\theta}\frac{\partial}{\partial\,\theta} - \frac{1}{\theta^2}\frac{\partial^2}{\partial\phi^2}\right) + \frac{1}{2}C\,\theta^2\,. \tag{13}$$

The latter is the Hamiltonian of a two dimensional harmonic oscillator if we identify θ with the polar radius. We denote by $\psi_{nm}(\theta,\phi)$ the eigenfunctions of the harmonic oscillator normalized in $0<\theta<\infty$, for which we adopt the notation of Ref. [5]. We obtain the Hamiltonian and the eigenfunctions for $\pi/2<\theta<\pi$ by the change $\theta\to\pi-\theta$. The (non-normalized) eigenfunctions of definite symmetry with respect to spin inversion in the entire range $0<\theta<\pi$ are

$$\psi_{nm\sigma}(\theta,\phi) = \frac{1}{\sqrt{2}}\left[\psi_{nm}(\theta,\phi)+\sigma\,\psi_{nm}(\pi-\theta,\pi+\phi)\right] + \delta\psi_{nm\sigma}(\theta,\phi)\,,\ \ \sigma=\pm 1 \tag{14}$$

where $\delta\psi_{nm\sigma}(\theta,\phi)$ is the distortion due to tunneling. They have eigenvalues

$$E_{nm\sigma}=\hbar\Omega\,(\,2n+|m|+1\,)-\frac{1}{2}\sigma\delta E_{nm} \tag{15}$$

where $\Omega=\sqrt{C/\mathcal{I}}=C\theta_0^2/\hbar$ and δE_{nm} is the energy splitting due to tunneling. We quote the values of θ_0 in other systems: $\theta_0^2\le 0.5$ in $LaMnO_3$ [5,6] while in the atomic nuclei of the rare earths [8] $\theta_0^2\approx 10^{-2}$.

The energy splitting of the ground state is very small, $\delta E\sim\hbar\Omega\exp\left(-2/\theta_0^2\right)$. Nevertheless for sufficiently low temperatures tunneling transitions will become important. This will happen when the tunneling temperature

$$T_t\approx\frac{\hbar\Omega}{k_B}\exp\left(-2/\theta_0^2\right) \tag{16}$$

is reached.

Region II, $E_\alpha >> C$, free rotor modes. At energies much higher than the potential barrier, but below the maximum energy k_BT_M, the nanoparticle will have the spectrum of a free rotor

$$E_l=\frac{\hbar^2}{2\mathcal{I}}l(l+1)\le k_BT_M\,. \tag{17}$$

Here the wave functions are the spherical functions whose spin-parity is $I_s\psi_{lm}(\theta,\phi)=(-)^l\psi_{lm}(\theta,\phi)\,.$

Region III, $E_\alpha\sim C$. In this region for $E_\alpha<C$ the states are characterized by tunneling, whose amplitude is no longer negligible, while the energy splitting can become comparable to the energy $\hbar\omega$. As a consequence the strongest dependence on the ac frequency should come from this part of the spectrum. Notice that we expect in our model two types of tunneling effects: those arising from region III of the spectrum at a temperature close to the blocking temperature, and those appearing at a temperature much smaller than the crossover temperature. Both types of effects give rise to a considerable complexity in the calculations. We avoid the tunneling effects at low temperature restricting ourselves to $T>T_t$, and those at higher temperature eliminating region III of the spectrum by extending the region I up to, and region II from, a *separation energy* k_BT_* such that

$$E=\begin{cases} E_{nm}\,, & E_{nm}<k_BT_* \\ E_l\,, & k_BT_*<E_l<k_BT_M\,. \end{cases} \tag{18}$$

In this way we renounce to derive the dependence of the susceptibility on the ac frequency, and we are forced to assume that $\hbar\omega << |E_\alpha-E'_\alpha|$ in the entire spectrum. We note that under such condition the function $\Phi_{\alpha,\alpha'}$ appearing in the expression of the susceptibility becomes symmetric.

We assume the *separation temperature* T_* as a phenomenological parameter.

Summarizing we have introduced the tunneling temperature T_t, the maximum temperature T_M and the separation temperature T_*. The crossover temperature in our model will be defined approximately in Eq.(30).

4. *Evaluation of the reactive susceptibilitiy.* We evaluate the longitudinal susceptibility, namely the response of the component of the magnetic moment along the ac magnetic field. Its average over the directions of the easy axis of the nanoparticle, namely over the directions of $\hat{\zeta}_1$ gives

$$\chi'=\frac{4}{3}\chi'_T+\frac{2}{3}\chi'_L \tag{19}$$

where χ'_T,χ'_L are the contributions arising when $\hat{\zeta}_1$ is respectively tranverse, parallel to the ac magnetic field

$$\chi'_T = \frac{1}{Z}\sum_{\alpha\alpha'}<\alpha|\sin\theta\cos\phi\,|\alpha'>^2\,\Phi_{\alpha,\alpha'}$$
$$\chi'_L = \frac{1}{Z}\sum_{\alpha\alpha'}<\alpha|\cos\theta\,|\alpha'>^2\,\Phi_{\alpha,\alpha'}\,. \tag{20}$$

The contribution of the free rotor modes turns out to be very small for reasonable values of the parameters, and therefore we neglect it in this preliminary report assuming $T_*=T_M$. Therefore the quantum number α represents only the oscillator quantum numbers (n,m) whose sums extend to $E_{nm}\le k_BT_*=k_BT_M$. It is convenient to introduce the parameters

$$\rho_C=\frac{C}{k_BT_*}\,,\ \ \rho_\Omega=\frac{\hbar\Omega}{k_BT_*}=\rho_C\theta_0^2\,, \tag{21}$$

the reduced temperature

$$x=\frac{T}{T_*} \tag{22}$$

and the constant

$$\chi_0=\mu\,\frac{\mu H_{ac}}{k_BT_*}\,\frac{1}{2\rho_C^2}\,. \tag{23}$$

After evaluation of the matrix elements to lowest order in θ_0 we get for the longitudinal part

$$\chi'_L(x)=\frac{1}{Z}\frac{1}{2}\rho_\Omega\chi_0\left[1-\exp\left(-\frac{2\rho_\Omega}{x}\right)\right]\sum_{n=0}^{1/(2\rho_\Omega)}(n+1) \times\sum_{m=-(1/\rho_\Omega-2n)}^{1/\rho_\Omega-2n}(n+|m|+1)\exp\left(-\frac{\rho_\Omega}{x}(2n+|m|)\right) \tag{24}$$

with a similar but longer expression for χ'_T that will be reported somewherelse. Performing the sums we get rather lengthy formulae, that will also be reported separately, but for numerical computations it is probably more convenient to use the above equation. The expression of the susceptibility, however, considerably simplifies for

$$\rho_\Omega / x \ll 1 \,. \tag{25}$$

Under such condition we can approximate the sums by integrals, getting

$$\chi'_T(x) = \chi_0 \frac{8}{3} \rho_C f_T(x) \;,\;\; \chi'_L(x) = \chi_0 f_L(x) \tag{26}$$

where

$$f_T(x) = g(x)^{-1} \left[1 - \left(1 + \frac{1}{x} + \frac{1}{2x^2} \right) \exp\left(-\frac{1}{x} \right) \right] \tag{27}$$

$$\begin{aligned} f_L(x) \;&=\; g(x)^{-1} x \left[1 - \left(1 + \frac{1}{x} + \frac{1}{2x^2} + \frac{1}{6x^3} \right) \right. \\ &\left. \times \exp\left(-\frac{1}{x} \right) \right] \end{aligned} \tag{28}$$

with

$$g(x) = 1 - \left(1 + \frac{1}{x} \right) \exp\left(-\frac{1}{x} \right) \,. \tag{29}$$

The exact expression of the susceptibility depends on 3 parameters: T_*, ρ_C, ρ_Ω. In the continuous approximation ρ_Ω disappears and we get a classical scaling because the susceptibility depends only on the classical parameters T_* and ρ_C. The functions $\chi_L(x)'/\chi_0, \chi_(x)'/\chi_0, \chi_(x)'_T/\chi_0$ are plotted in Fig.2 for $\rho_C = 0.015$, chosen to have a typical shape of the nanoparticle susceptibility. Because ρ_Ω must be of the order of ρ_C or smaller, such a value justifies the approximation of sums by integrals. This is confirmed by the comparison, in Fig. 3, of the exact and continuous approximation of $\chi_L(x)/\chi_0$.

According to the condition (25), however, such approximation will only be valid for reduced temperatures

$$x \gg x_c = \frac{T_c}{T_*} \approx \rho_\Omega \,. \tag{30}$$

Because above x_c the energy can be approximated by a continuous variable, while below the quantum spectrum must be used, x_c is the reduced temperature of crossover from classical to quantum behavior. The above equation, however, provides only an estimate of x_c because its exact value should be found by determining the inflection of χ'.

Below the crossover down to the tunneling reduced temperature we must use the exact expression of the susceptibility (24). We can check analytically that the functions χ'_L and χ'_T are approximately constant for small x. Now $x_t \approx x_c \exp(-2/\theta_0^2)$, and since θ_0^2 must be not greater than 1 for the macrospin to be polarized, $x_t \ll x_c$ and we can approximate the susceptibilities at $x = 0$ with their values at x_t

$$\chi'_L(x_t) \approx \chi'_L(0) = \frac{1}{2} \rho_\Omega \chi_0 \,,\;\; \chi'_T(x_t) \approx \chi'_T(0) = \frac{8}{3} \rho_C \chi_0 \tag{31}$$

where $\chi'_L(0), \chi'_T(0)$ are the exact values neglecting tunneling. By comparison with Eqs.(26)-(29) we see that the continuous approximation is valid for χ'_T up to small temperatures, but instead the exact expression of χ'_L, at variance with (26), does depend on ρ_Ω, a quantum parameter, and does not go to zero. In Fig. 3 we see that for $\rho_\Omega = 0.007$ the exact expression of χ'_L/χ_0 and its continuous approximation to deviate from each other for $x \leq 0.01$, namely $T_c \approx 0.01 T_*$. Such a value of the reduced temperature decreases with decreasing ρ_Ω.

One observation is in order here. The continuous approximation should become more accurate with increasing x, which apparently is not the case in the plot of Fig.3 in which the difference with respect to exact expression remains approximately constant. In order to understand this fact let us consider as an example the partition function Z(x). Its limit for $x \to \infty$ at fixed ρ_Ω, which is what we can see in the plot, is

$$Z_{exact}(\infty) = \frac{1}{2\rho_\Omega^2} + \frac{1}{2\rho_\Omega} + 1 \,, \tag{32}$$

while the limit of the continuous approximation is

$$Z_{continuous}(\infty) = \frac{1}{2\rho_\Omega^2} \,, \tag{33}$$

because in such an approximation only the leading term in ρ_Ω^{-1} survives. Therefore increasing x, $Z_{exact}(x) \to Z_{continuous}(x)$ only for $\rho_\Omega \to 0$. The reason is that the functions appearing in the expression of the susceptibility are not functions of ρ_Ω/x, because the range of the sums depends only on ρ_Ω.

We checked that for $\rho_\Omega \to 0$ the continuous approximation exactly reproduces all the exact functions. We remark that the coincidence of the plots for $0.01 < x < 0.2$ is only accidental.

5. *How to compare with experiment.* The susceptibility depends on the volume of the nanoparticles. In our model such dependence is contained in the moment of inertia $\mathcal{I}$, the restoring force constant C and the separation temperature T_*. The theoretical determination of these parameters is beyond the scope of the present paper.

Concerning the dependence of the susceptibility on the nanoparticle volume it is important to remember that in the scaling region, namely for $T > T_c$, χ' depends only on ρ_C and T_*. Now it is reasonable to assume that C is proportional to the volume. Moreover, since T_* is approximately the temperature at which the macrospin becomes a free rotor, it should be proportional to the potential barrier C, and therefore also proportional to the nanoparticle volume v, so that ρ_C should not depend on it. Under this assumption, in the scaling region the susceptibility depends on the volume only through T_*,

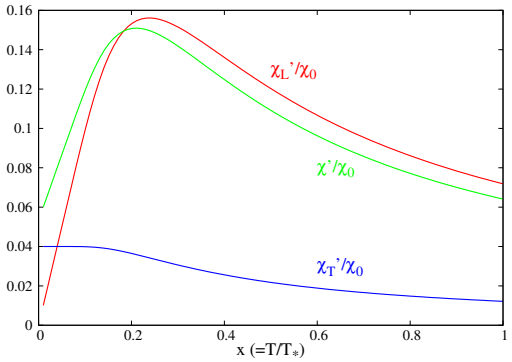

FIG. 2: The continuous approximations of the functions $\chi'_L(x)/\chi_0$ (red, upper line), $\chi'(x)/\chi_0$ (green, middle line) and $\chi'_T(x)/\chi_0$ (blue, lower line) versus the reduced temperature x for $\rho_C = 0.015$.

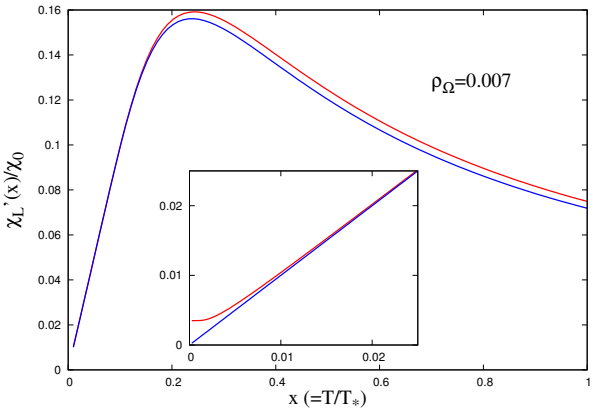

FIG. 3: The continuous approximation of the function $\chi'_L(x)/\chi_0$ (blue, lower line) compared with the exact expression (red, upper line) for $\rho_\Omega = 0.007$. The inset shows that they depart from each other for $x \leq 0.01$.

that appears in the denominator of the constant χ_0 and implicitly in the reduced temperature x. We therefore define the function

$$\eta(v) = \frac{T_*(\overline{v})}{T_*(v)} \tag{34}$$

where $\overline{v}$ is the average volume of nanoparticles in a sample. The function

$$\Phi = \eta f_L(\eta\, x) \tag{35}$$

is proportional to the susceptibility (neglecting for simplicity the small transverse contribution) of nanoparticles of volume v. In practice therefore one should parametrize T_* in terms of the volume, average the susceptibility over the volume distribution of a given sample and fit the parameters. In Fig.4 we show the function Φ for different values of η.

In the following we assume that the dispersion in volume is so small that the weighted average has a negligible

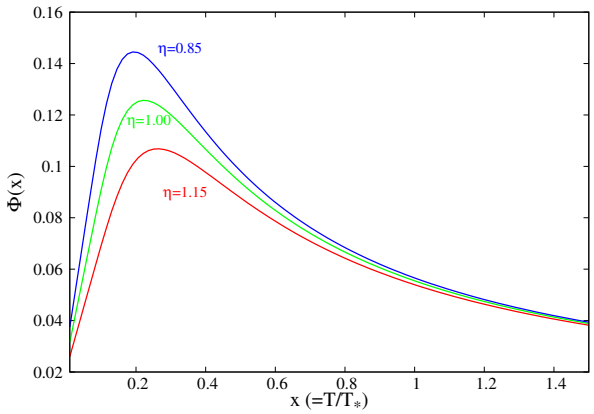

FIG. 4: The function $\Phi(x)$ for $\rho_C = 0.007$ and $\eta = 0.85, 1.00, 1.15$ (upper, blue; middle, green; lower, red, lines resp.)

effect. In such a case

1) the temperature $T_* = T/x$ can be evaluated for $x = x_B$, the reduced temperature at which χ' has a maximum, determined theoretically, and the corresponding experimental value T_B

2) ρ_C can be determined by fitting the experimental susceptibility above the crossover temperature

3) ρ_Ω can be determined by fitting the experimental susceptibility on a range of temperatures extending below the crossover. From ρ_C and ρ_Ω we can derive the value of $\theta_0^2 = \rho_\Omega/\rho_C$ and then of the moment of inertia

4) the crossover temperature $T_c = \rho_\Omega T_*$ is then determined and can be compared with the value x_c at which χ' has an inflection

5) the tunneling temperature $T_t = \rho_\Omega T_* \exp(-2\rho_C/\rho_\Omega)$.

We quote a number of examples [23],[26],[27], without attempt to completeness, in which the susceptibility has a form that appears to us compatible with our model. In these experiments the blocking temperature is at most of the order of one hundred degrees, so that T_* is a few hundreds degrees or smaller. For typical values of $\rho_\Omega \sim 0.005$ according to Eq.(30) T_c is of the order of 1 K or smaller, as we can infer also from the comparison of Fig. 3. We notice that our typical values of $\rho_\Omega \approx \rho_C$ imply $\theta_0^2 \approx 1$. By comparison we quote the value of $\theta_0^2 = 0.5$ we estimated [5,6] for $LaMnO_3$.

Finally we wanted to make a comparison with some experimental results. We looked for the case of a sample in which the nanoparticles could be considered to a reasonable approximation noninteracting. We choosed the data of Ref.[27], that refer to γ-Fe_2O_3 nanoparticles of spherical shapes with a mean diameter of 7 nm and a volume concentration of 0.3%. Their clusterization was prevented by coating them with a surfactant layer. Moreover, since the nanoparticles were suspended in a hydrocarbon oil, at low temperatures the oil froze and the nanoparticles were randomly distributed in the sam-

ples. In Fig. 5 we compare our theoretical susceptibility with the experimental one. Because the data do not extend such low temperatures that a crossover is visible, we adopt for simplicity the continuous approximation with $\rho_C = 0.007$. We deem the agreement is remarkable, even if we must remember that the theoretical susceptibility is not averaged over the nanoparticle size distribution. We emphasize that the theoretical expression depends on 2 parameters only, ρ_C and T_*.

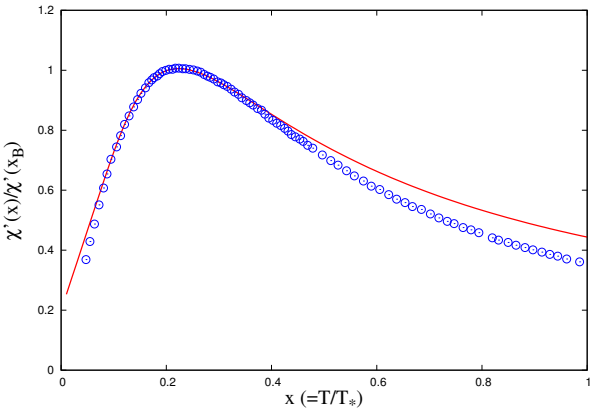

FIG. 5: The experimental susceptibility (lower, blue line) and the theoretical one in the continuous approximation (upper, red line) for $\rho_C = 0.007$ normalized to their maximal values. The experimental data are from Ref.[27], assuming $T_* \approx 100K$.

Our model cannot certainly have a universal validity. There are of course results that cannot be reproduced by it. We quote 2 examples. In the nanoparticles studied in Ref. [28] there are 2 magnetic atoms, namely TM and RE, in the ones of Ref. [29] there are different phases. No wonder that our model, in which the macrospin is assumed to have a uniform structure, cannot reproduce these data.

6. *Conclusions.* We have constructed a model of magnetic nanoparticles in which the moment of inertia of the macrospin appears naturally. The model is designed for nanoparticles in which the constituent spins are locked to the density profile of the macrospin, but because of the apparently general agreement with typical experimental data it might have a wider validity as an effective model. It seems therefore important to us to perform a detailed accurate screening of experimental data, taking into account the dispersion in size in any sample, to establish whether there exists a specific kind of nanoparticles characterized by spin-orbit locking. For such nanoparticles the orbital contribution to the susceptibility, that we neglected but can easily be included, might be significant.

In our model tunneling is obviously important at very low temperatures, $T < T_t$, and possibly important at temperatures of the order of the separation temperature T_*, namely the temperature at which the modes of the macrospin change from harmonic oscillator to free rotor. We deem tunneling is essential for a proper description of the dependence of the susceptibility on the ac frequency of the applied magnetic field. We neglected for simplicity this contribution, and this is the only approximation, although an important one, in the evaluation of the susceptibility for $T > T_t$.

We find for several kind of nanoparticles a crossover temperature T_c of the order of 1K, below which quantum hopping is important and above which thermal hopping dominates. Above T_c to a very good approximation the dependence on the moment of inertia disappears and the susceptibility exhibits a classical scaling.

Acknowledgment

We are grateful to D. Di Gioacchino for many interesting discussions. Authors acknowledge the financial support of the Bilateral Cooperation Agreement between Italy and India of the Italian Ministry of Foreign Affairs (MAE) in the framework of the project of major relevance *Investigating local structure and magnetism of cobalt nano-structures.*

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