Thermodynamics of Two Dimensional Magnetic Nanoparticles.

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A two dimensional magnetic particle in the presence of an external magnetic field is studied. Equilibrium thermodynamical properties are derived by evaluating analytically the partition function. When the external field is applied perpendicular to the anisotropy axis the system exhibits a second order phase transition with order parameter being the magnetization parallel to the field. In this case the system is isomorph to a mechanical system consisting in a particle moving without friction in a circle rotating about its vertical diameter. Contrary to a paramagnetic particle, equilibrium magnetization shows a maximum at finite temperature. We also show that uniaxial anisotropy in a system of noninteracting particles can be misinterpreted as a ferromagnetic or antiferromagnetic coupling among the magnetic particles depending on the angle between anisotropy axis and magnetic field.

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The remarkable development of experimental techniques grants increasingly more access to the hitherto mysterious nanometric world. In the particular case of magnetism, a recent experimental study has succeeded to investigate single clusters of around 3 nm diameter, using a special micro-SQUID device \cite{1}. Also, a wide variety of magnetic microscopies \cite{2,3} are under constant development to measure the magnetization process of single clusters in the nanometer range. In this context, the classical Stoner-Wohlfarth (SW) \cite{4} model has been frequently revisited, to test whether or not such simplistic uniform rotation model really provides a realistic picture of the magnetization reversal of a nanoparticle \cite{4,5}. The SW model does not take explicitly into account thermal fluctuations, and therefore it is strictly valid for very low temperatures or very strong anisotropies \cite{4,5}. On the other hand, when the anisotropies are rather small and/or the temperatures are sufficiently high, the so-called superparamagnetic approach must be employed. In such case, Néel \cite{6} and Brown \cite{7} introduced the idea that the decay toward a thermal equilibrium state of the magnetic moment of a single-domain ferromagnetic nanoparticle is mediated by thermal fluctuations, following a simple Arrenhius switching probability \cite{7,12}. Also in this case, further improvements of the model have been introduced year after year in order to include additional terms which are usually present in real samples, such as anisotropy \cite{13,14,15} and dipolar interaction among magnetic nanograin \cite{16,17}.

In this letter, we present a mechanical analog to a magnetic moment in the presence of an external field perpendicular to its uniaxial anisotropy axis. This particular system exhibits a second order phase transition as a function of the external field, where the order parameter is the magnetization. Its thermodynamics is also analytically solved showing the behavior of the magnetization and susceptibility as a function of temperature. Finally we demonstrate that uniaxial anisotropy in an ensemble of non interacting SW particles can be misinterpreted as a ferro or antiferromagnetic coupling among the particles.

Let us consider a single magnetic domain particle with all its atomic moments rotating coherently on a plane in the presence of an external magnetic field. The particle is characterized by a constant absolute value of the magnetization $m = m_s V$, $V$ being the volume of the particle and $m_s$ its saturation magnetization. Well below the Curie temperature of the specific magnetic element, $m_s$ is independent of particle volume and temperature. The energy of this nanoparticle has three contributions: anisotropy energy, either due to shape, stress or crystalline structure of the particle; Zeeman energy, owing to the presence of an external field, $\hat{H}$, and the magnetic dipolar interaction among the atoms composing the grain, and which will not be considered in the present work. Under these conditions the energy reads:

$$E = - \vec{m} \cdot \vec{H} - \kappa V \left( \frac{\vec{m} \cdot \hat{n}}{m} \right)^2 ,$$

where $\kappa$ is the anisotropy constant and the unit vector $\hat{n}$ represents the easy magnetization direction. We will initially focus on the particular case in which the external field is perpendicular to the anisotropy axis. Then, the energy of the single particle can be written as:

$$E = - m H \cos \theta - \frac{1}{2} m H_a \sin^2 \theta ,$$

where we have defined the anisotropy field $H_a$ such that $\kappa V = \frac{1}{2} m H_a$ and $\theta$ represents the angle between magnetization and external field.
A more suggestive form is obtained by making the energy dimensionless as follows:

\[
\mathcal{E} = \frac{E}{mH} = -\cos \theta - \frac{1}{2} \frac{H_a}{H} \sin^2 \theta .
\]

Now, let us consider a rigid circular ring of radius \( R \) rotating along its vertical diameter at angular frequency \( \omega \) with a frictionless particle of mass \( m \) free to move on the ring, as illustrated in Fig. 1. The particle is under gravity, \( mg \), and normal force \( \bar{N} \) due to the ring, which is rotating, and therefore the mass describes a circular orbit due to the centripetal acceleration originated from the horizontal component of \( \bar{N} \). By choosing the zero level of gravitational energy at the center of the ring, the Lagrangian for this system reads

\[
\mathcal{L} = \frac{1}{2} mR^2 \dot{\theta}^2 + \frac{1}{2} m\omega^2 R^2 \sin^2 \theta + mgR \cos \theta .
\]

Last equation can be rewritten as \( \mathcal{L} = T - U \), with \( T \) being the kinetic energy and \( U \) an effective potential energy that includes the effects of gravity and the rotation of the system. Introducing a dimensionless form one finds that

\[
U = \frac{U}{mgR} = -\cos \theta - \frac{1}{2} \frac{R \omega^2}{g} \sin^2 \theta .
\]

Therefore the analogy between this mechanical system and the magnetic particle describes by Eq. 1 is clear. The centripetal acceleration, \( R \omega^2 \), plays the role of the magnetic anisotropy whereas the gravity field is equivalent to the external magnetic field. Obviously, the downwards component can be further increased by means of the application of an additional force, and in such case the total force \( F \) divided by the mass of the particle represents the applied field. Notice that achieving the anisotropy field is equivalent to apply a downwards force which completely compensates the vertical component of the normal force on the particle.

When we analyze this mechanical system, a second order phase transition appears. Analogously, analyzing the magnetization along the field as a function of the parameter \( H_a/H \), a second order phase transition is clearly observed. In the latter case, the order parameter is the angle \( \theta \). Figure 2 shows the energy as a function of \( \theta \) for two different values of \( H_a/H \). Clearly, there is a smooth transition between one minimum in the energy landscape, for \( H_a/H < 1 \), to two minima, for \( H_a/H > 1 \). The transition occurs for an external field strong enough to make the equilibrium state a magnetized one along the field. On the other hand, when the anisotropy field is stronger, there are two minima. They correspond to the states with non zero magnetization component along the uniaxial anisotropy axis together with the magnetization component along the external field. Then, there is a second order phase transition for \( H_a/H = 1 \), in analogy with the well-known SW predictions.
Figure 3 illustrates the order parameter $\theta$ as a function of the ratio $H_a/H$. The second order phase transition is clearly evidenced. This figure also illustrates the position-frequency phase diagram for the mechanical analog depicted in figure 1.

Now we investigate the thermodynamic of this particular system in the canonical ensemble. The partition function $Z_{2D}$ reads:

$$Z_{2D} = \int_0^{2\pi} d\theta \exp \left( \frac{mH \cos \theta + \frac{1}{2}mH_a \sin^2 \theta}{kT} \right).$$

This integral can be analytically solved and the result can be written as a series in Bessel functions of integer argument.

$$Z_{2D} = 2\pi \sum_{n=0}^{\infty} \left( \frac{2n}{n} \right) \left( \frac{H_a}{4H} \right)^n I_n \left( \frac{mH}{kT} \right).$$

By making $H_a = 0$ we recover the ideal case of a paramagnetic system in 2D. Hereafter thermodynamics follows and it can be computed analytically. Magnetization and susceptibility of the particle along the field are respectively given by

$$< m > = kT \frac{\partial \ln Z_{2D}}{\partial H} ; \quad \chi = \frac{\partial < m >}{\partial H}.$$

These formula are evaluated using the recurrence relations for the first derivative of the Bessel functions.

Figure 4 illustrates the magnetization along the external field as a function of temperature for a system of non interacting particles with $m = 1000\mu_B$ each and external field $H = 0.1kOe$. At $T = 29.6K$ the magnetization exhibits a maximum for $H_a/H = 30$. This behavior is clearly understood by using the mechanical analog, where at fixed rotation speed $\omega$ and zero kinetic energy, the equilibrium angle $\theta$ is larger than the value obtained by a small increasing of kinetic energy in the particle, due to the asymmetry of the energy landscape around a minimum. Further increasing in kinetic energy makes the angle increases up to an asymptotic final value of $\theta = \pi/2$.

In our magnetic system, larger kinetic energy corresponds to higher temperatures. Therefore, in equilibrium and for $H_a/H > 1$, the magnetization exhibits a maximum at a temperature $T$ such that $kT = 0.152(H_a/H - 1)mH$.

Figure 5 displays the magnetic susceptibility along the field direction as a function of temperature. The broken line depicts results for $H_a/H = 0.9$ and the continuous line for $H_a/H = 30$. In the region of the double well potential, $H_a/H > 1$, one clearly observes a maximum in both magnetization and susceptibility curves.

The maximum of the susceptibility for $H_a/H << 1$ approximately occurs at a temperature $T_{max}$ given by $mH/kT_{max} = 1.33$, which corresponds to the value for a paramagnetic particle in 2D. For $H_a/H = 30$, the maximum occurs at $mH/kT_{max} = 1.0$.

Finally, in order to explore the role of anisotropy, Figure 6 illustrates the inverse susceptibility for different angles $\alpha$ between anisotropy axis and external magnetic field. For a parallel orientation between anisotropy axis and magnetic field we observe a susceptibility curve resembling a ferromagnetic system.
The system of non-interacting magnetic particles with parallel anisotropy axes under the presence of an external field applied perpendicular to the anisotropy axes exhibits (at \( T = 0K \)) a second order phase transition as a function of the ratio between external field to the anisotropy field. The order parameter being the magnetization of the system. Such system is isomorph to a mechanical system consisting in a particle moving without friction in a circle rotating about its vertical diameter. At finite temperature the thermodynamics of the system can be solved analytically and the magnetization along external magnetic field shows a maximum at a finite temperature, contrary to that of a paramagnetic particle. The inverse susceptibility of a system of non interacting magnetic particles as a function of temperature demonstrates that uniaxial anisotropy acts similarly to effective ferromagnetic or antiferromagnetic coupling, depending on the angle between magnetic field and anisotropy axis. The presented results can be useful in the interpretation of magnetic data obtained in nanocrystalline materials, specially novel artificially grown patterned media for high density magnetic recording, which, depending on the aspect ratio, can display a strong 2D character.

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