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Thermodynamics of three-dimensional magnetic nanoparticles

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Abstract

A three-dimensional system of non-interacting nanoparticles with uniaxial anisotropies is studied. Equilibrium thermodynamical properties are derived by evaluating the partition function. When 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. Contrary to a superparamagnetic particle, the magnetization shows a maximum at finite temperature. Moreover, it is found that the magnetic susceptibility considerably deviates from Curie law. This can be misinterpreted as a ferromagnetic or antiferromagnetic coupling among magnetic particles, depending on the angle between the anisotropy axes and the external magnetic field.

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The nanometric world increasingly gains access due to the remarkable development of experimental techniques. In the particular case of magnetism of nanoparticles, recent experimental study has succeeded in investigating single clusters of around 3 nm diameter, using special micro-SQUID device [1]. In this letter, we report the study of non-interacting three-dimensional nanoparticles having the same uniaxial axis. Each particle is considered as a ferromagnetic monodomain with magnetic moment m. The energy of a each particle is given by (Zeeman and anisotropy energy terms)

$$E = -\vec{m}\cdot\vec{H} - \frac{1}{2}mH_a\left(\frac{\vec{m}\cdot\hat{n}}{m}\right)^2, \tag{1}$$

where $\vec{H}$ is the external field, H_a is the anisotropy field and $\hat{n}$ is the anisotropy axis. In the particular case of external field along the z-axis, $\vec{H} = (0,0,H)$, and anisotropy axis along the x-axis, $\hat{n} = (1,0,0)$, we have

$$E = -mH\cos\theta - \tfrac{1}{2}mH_a\sin^2\theta\cos^2\phi, \tag{2}$$

ϕ and θ being the azimuthal and polar angles of the magnetization vector, $\vec{m} = m(\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$. Therefore, in this particular case the partition function reads

$$\mathbb{Z} = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \times \exp\left(\frac{mH}{kT}\cos\theta + \frac{mH_a}{2kT}\sin^2\theta\cos^2\phi\right). \tag{3a}$$

The last integral can be solved more convenient by choosing the z-axis as the anisotropy easy axis, and the external field along the x-axis. In that case, the above integral reduces to

$$\mathbb{Z} = \frac{1}{4\pi}\int_0^{2\pi} d\phi \int_0^{\pi} d\theta \sin\theta \times \exp\left(\frac{mH}{kT}\sin\theta\cos\phi + \frac{mH_a}{2kT}\cos^2\theta\right) \tag{3b}$$

and finally the closed form

$$\mathbb{Z} = (2\pi)^{3/2}\sqrt{\frac{kT}{Hm}} \times \sum_{n(\text{even})}^{\infty} \frac{(2n)!}{(2^n n!)^2}\left(\frac{H_a}{H}\right)^n I_{n+1/2}\left[\frac{mH}{kT}\right]. \tag{4}$$

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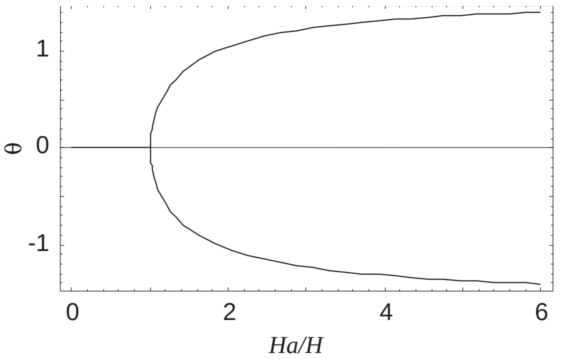

Fig. 1. Equilibrium angle, θ, between magnetization and external field, as a function of the ratio H_a/H.

Therefore, the magnetization along the magnetic field is given by the following expression:

$$M = m\frac{\partial \ln Z}{\partial \xi} \quad \text{where} \quad \xi = \frac{mH}{kT}. \tag{5}$$

For the cases of arbitrary angle between external field and anisotropy axes, it is preferable to evaluate the integrals numerically. The results of equilibrium magnetization as a function of the ratio H_a/H for different azimuthal angles is shown in Fig. 1. The azimuthal angle which minimizes the energy of Eq. (2) is $\phi = 0$. A second-order phase transition is observed, the order parameter being the magnetization along the magnetic field. The same result is obtained for the 2D case [2].

The next graph (Fig. 2) depicts the result of the magnetization (in Bohr magnetons) as a function of temperature (in Kelvin), evaluated using Eq. (5), with the following parameters, $m = 1000\,\mu_B$, $H_a = 3$ kOe, and $H = 0.1$ kOe.

Fig. 3 illustrates the inverse susceptibility for different angles between the anisotropy axis and external field. For a parallel orientation between anisotropy axis and magnetic field (dotted line), one observes a susceptibility curve resembling a system with ferromagnetic-like interactions. However, for perpendicular orientation between magnetic field and anisotropy axis (long dashed line), a typical Curie–Weiss antiferromagnetic-like behavior is observed. For 45° (dashed line), the system still resembles a ferromagnetic behavior. This is a marked difference with respect to the same system in the 2D case, which at 45° behaves like a paramagnetic particle [2]. The continuous line shows the result for an ideal paramagnetic particle.

Concluding, we demonstrated that in the 3D case, a free magnetic particle with uniaxial anisotropy has a magnetization maximum at finite temperature when the external field points perpendicular to the easy axis. Moreover, the behavior shown in the magnetic susceptibility deviates from the result of an ideal superparamagnetic particle, resembling ferro or antiferromagnetic behavior depending on the relative orientation of the anisotropy axis and external field. These results can be useful in the interpretation of magnetic data obtained for nanocrystalline particles and where the interparticle interaction can be neglected.

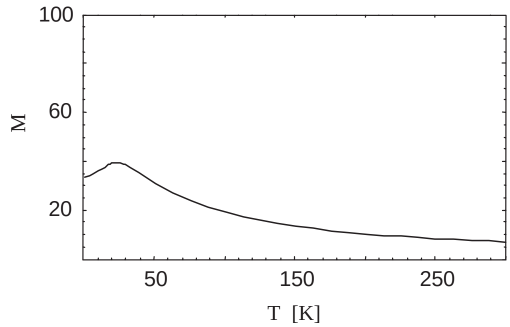

Fig. 2. Magnetization along the external field (units of μ_B) as a function of temperature (in Kelvin) for a free 3D magnetic nanoparticle with $m = 1000\,\mu_B$. The external field is $H = 0.1$ kOe and perpendicular to the easy axis. The anisotropy field is $H_a = 3$ kOe.

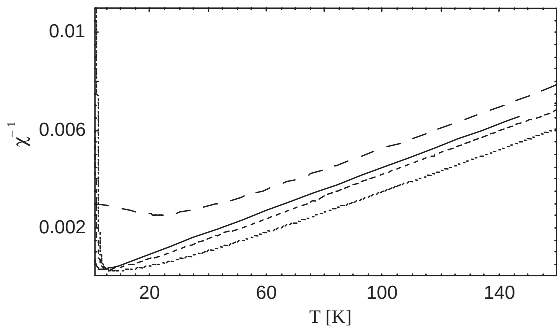

Fig. 3. Inverse magnetic susceptibilities along the external field (units of kOe/μ_B) as a function of temperature (in Kelvin) for a free 3D magnetic nanoparticle with $m = 1000\,\mu_B$. The external field is $H = 0.1$ kOe and anisotropy field is $H_a = 3$ kOe. The broken curves represent different angles between anisotropy axes and external field (see text). The full line curve depicts the result of an ideal superparamagnetic particle.

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