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Comment on "Generalized Stoner-Wohlfarth Model and the Non-Langevin Magnetism of Single-Domain Particles" by M. A. Chuev

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In this work we analyzed the model by M. A. Chuev recently published [JETP Letters **85**, 611 (2007)]. Near the blocking temperature we show that the anisotropy corrections always lead to a lower magnetization than the equilibrium value, contrary to the findings in Chuev's work. Also we show that the asymptotic high-temperature limit of Chuev's model is not in agreement with the expected thermodynamic limit. Moreover, even at low-temperature only a careful implementation of this theory can guarantee arriving to the correct result, avoiding some wrong conclusions in Chuev´s work.

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Recently Chuev [1] presented a generalization of the Stoner-Wohlfarth (SW) model to describe the thermal effect on the dynamics of an ideal non-interacting nanoparticle ensemble. In the model, Chuev incorporated a thermally-assisted transition-probability into the SW formulation [2] (Eq. (2) of reference [1]). However, his low temperature (T) implementation is incorrect and from these results he arrives to a serious conceptual error. Besides, the model is not applicable to the high-T limit, because it does not follow the expected thermodynamic behavior.

We want to start the treatment of the Chuev model showing his basic assumptions. In the model, based on the SW one, the magnetic energy of a non-interacting single particle is given by:

$$E = -\mu_0 H \sin\varphi - K\cos^2(\theta - \varphi), \qquad (1)$$

where K is the magnetic anisotropy constant, θ is the angle between the magnetic field orientation and the easy axis of the particle, and φ is the angle between the magnetic moment μ and the external field H. The thermal information is introduced considering the Néel formula [2] of the probability of transition (per unit of time) from one minimum to the other:

$$p_{12,21}(H,\theta,\varphi) = \frac{p_0}{2}\sum_{i=1,2} e^{-\left(E_i^{max} - E_i^{min}\right)\beta}, \qquad (2)$$

where $\beta = 1/k_B T$ (thermal energy), p_0 is a constant characteristic for each material that is weakly dependent of the temperature and is typically of $10^9 - 10^{11}$ [1/s], $E_i^{\max}$ and $E_i^{\min}$ are the energies of the maximum and minimum respectively determinate by eq.(1).

The temporal change in the non-equilibrium populations of the local states $w_i(t)$ is determined using the master equation (eq.(6) in reference [1]):

$$\frac{dw_{1,2}(t)}{dt} = \pm[p_{21}(t)w_2(t) - p_{12}(t)w_1(t)]. \qquad (3)$$

From these expressions it is possible to simulate the field cooling (M_{FC}) and zero filed cooling (M_{ZFC}) magnetizations, assuming a constant temperature sweep ratio.

Before continuing, we want to remark that this model includes the information about the thermal inversion of the magnetization as well the temporal evolution of the population at each minimum by the expression (2) and (3) respectively. However, this model does not consider the effect of the thermal fluctuation in each minimum of eq.(1). We think this omission may be not relevant at low-T, as the magnetic moment orientation probability away from the minima is negligible. However, this simplification can not be maintained at high-T where the thermal fluctuations dominate.

Figure 2 of reference [1] shows the simulation of PFC (M_{FC}), ZFC (M_{ZFC}) and NFC (negative M_{FC}). The dot line corresponds to the Langevin function. About this figure Chuev said "...the magnetization in the PFC and NFC regimes is larger and smaller than the equilibrium value, respectively." In this observation we found two serious conceptual errors. The first one is that M_{FC} below the blocking temperature, T_B, is always lower than the equilibrium magnetization value. To illustrate this we simulated (Fig.1) M_{FC} and M_{ZFC} using the

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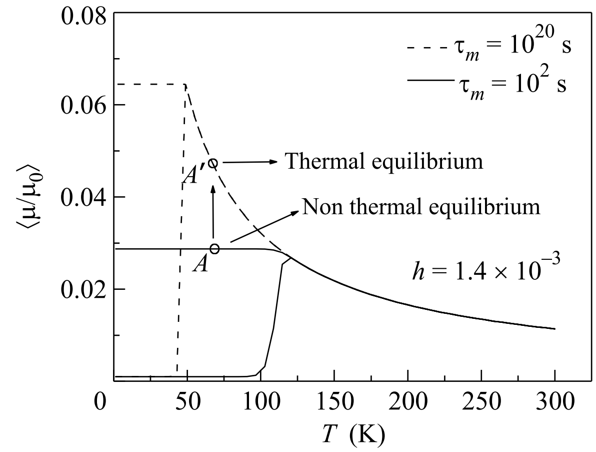

Fig.1. M_{FC} and M_{ZFC} simulated using the Chuev model. Increasing the temporal windows the point A reaches the thermal equilibrium increasing the magnetization

model described in reference [1], considering the angular average over the easy axes orientation as pointed out in eq.(11) of [1], for different temporal windows τ_m.

It is possible to see that the point labeled A is not in thermal equilibrium for $\tau_m = 10^2$ s. However, increasing the temporal window ($\tau_m = 10^{20}$ s) the system reaches equilibrium at the given temperature, increasing its magnetization (A'), contrary to Chuev observation. We can also observe that M_{FC} is almost constant below T_B, as expected for an ideal ensemble of identical and non-interacting nanoparticles. Chuev calculations shown on Fig.2 of reference [1] does not follow this behavior, increasing the magnetization value with the temperature decreasing below T_B.

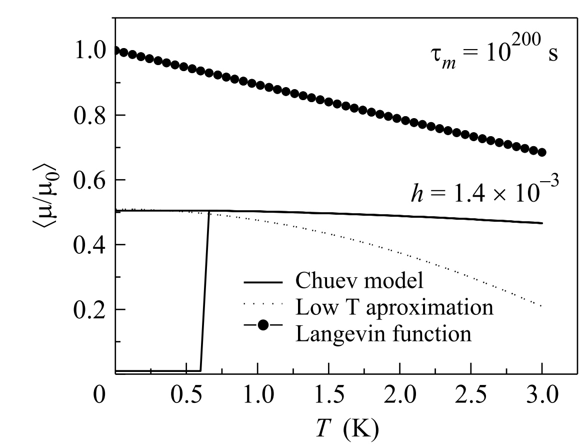

Fig.2. Full line: M_{FC} and M_{ZFC} simulation using the Chuev model. Dash line: low temperature approximation (see eq.(4)). The dots correspond to the Langevin function

The second error that we mentioned before is that the Langevin curve does not represent the thermal equilibrium condition in a system which has a not negligible anisotropy, even considering an easy axis random distribution. Although Chuev does not explicitly mention this, fig.2 and also the commentary associated to it, indicates that this is the intention of the author. We will return to this point later, when we consider the high temperature limit. Now we want to show that the low temperature limit, assuming thermal equilibrium, in Chuev's model has a different behavior than the associated to the Langevin equation. We consider the case: $K \gg \mu_0 H \gg k_B T$ (μ_0 is the magnetic moment of the particle). In this approximation we found that the thermal equilibrium magnetization (assuming that the temporal window is large enough for arriving to thermal equilibrium) in the Chuev model (considering the average over the easy axis random distribution) follows the expression:

$$\left\langle \frac{\mu}{\mu_0} \right\rangle \approx \frac{1}{2} + \frac{\mu H}{3K} + \frac{3}{x^2}\left[e^{-2} \quad (1+2x) - 1\right], \qquad (4)$$

where $x = \mu H / k_B T$.

On the other hand the correspondent expression of the Langevin function is:

$$\left\langle \frac{\mu}{\mu_0} \right\rangle \approx 1 - \frac{1}{x} + 2e^{-2x}. \qquad (5)$$

In Fig.2 we show simulations of M_{FC} and M_{ZFC} made using the Chuev model, the low temperature approximation obtained in (4) and the Langevin function at very low temperatures, in order to illustrate our concept.

We can see in this figure the clear difference in the low temperature range, assuming thermal equilibrium. The temporal window used was $\tau_m = 10^{200}$ s, large enough to get the system in the superparamagnetic regimen yet at very low temperature. We believe that the origin of the erroneous result shown in Fig.2 of [1] is due to the initial conditions imposed by the author in equation (9). Only the initial condition of the M_{ZFC} it is correct because is true that the initial magnetization is null for an ideal no interacting nanoparticle system. The others (1 and −1) are wrong because they depend of the applied magnetic field. In fact, it could be possible, in theory, to have initial condition 1 or −1, but in these cases the field should be so strong (erasing all energy barrier effects, and then getting only one minimum) that the PFC and NFC would not exhibit irreversibility.

We consider now the high temperature behavior in Chuev model. In first place, it is important to know which is the expected asymptotic magnetic response in the high temperature limit, ie. when $k_B T \gg K$, μ_0 H.

In this treatment we will assume that, for a given experimental temporal window τ_m, the temperature is high enough to let the magnetic moment oscillate between *both* energy minima. In this condition the system is in thermal equilibrium and the complete statistical information is contained on the partition function Z [3]. According the treatment given by the Statistical Mechanics, the value of the magnetization, for a given H and T is given by the expression:

$$\langle \mu \rangle = \frac{1}{Z} \int_{\Omega} \mu_H \, e^{-\beta E(\Omega)}, \qquad (6)$$

where μ_H is the magnetic component along the external magnetic field orientation, $E(\Omega)$ represents the magnetic energy (see eq.(1)) for a given set of Ω parameters. In this case Ω space is (θ, φ) magnetization orientation angles, and the integration is carried over all possible angles. Z is the partition function given by:

$$Z = \int_{\Omega} e^{-\beta E(\Omega)}. \qquad (7)$$

It is not possible to obtain a close analytical expression for (7). But we can expand this expression in the Taylor series on the high temperature approximation. Making this and integrating over all anisotropy angles (assuming a random orientation distribution) as is indicated on eq.(11) of [1], we finally obtain:

$$\left\langle \frac{\mu}{\mu_0} \right\rangle \approx \frac{x}{3} - \frac{x^3}{45} + \frac{2x^5}{945} - \frac{8x^3 K^2}{10125}\beta^2 + \ldots \qquad (8)$$

This means that the high-T description, should follow eq.(8), as found on references [4, 5]. In the expression (8) we can see that the first three terms on the right hand member correspond exactly to the Taylor expansion of the Langevin function. The last one corresponds to the correction introduced by the anisotropy effect. We can see that this term (quadratic in K) is negative, then in the high temperature limit, the magnetization of a given nanoparticle system (in thermal equilibrium) is always *lower* than the associated Langevin function. Morower, we want to point to the fact that, in the high temperature limit, the magnetization goes asymptotically to zero as the Langevin function. Returning to the Chuev model, we can see in eq.(20) of [1] the high temperature limit (rewritten in terms of the normalized magnetization):

$$\left\langle \frac{\mu}{\mu_0} \right\rangle \approx \frac{x}{3} + \frac{\mu_0 H}{3K} + \ldots \qquad (9)$$

The first term of the right of (9) is in accord wich (8). However, the second one is indicating that the magnetization does not go to zero in the high-T limit, *i.e.* it does not satisfy the thermodynamic limit. This is a serious problem for this formulation, and for this reason we have serious doubts about the results shown in fig.3 and 4 of [1] as well as the conclusions associated to them. In our fig.3 we show the normalized magnetization obtained

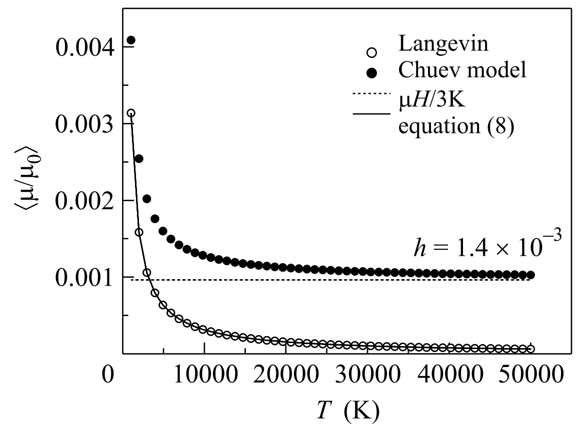

Fig.3. Limit of high temperature behavior for the Chuev model (full dot) and Langevin function (open dot). The solid line corresponds to eq.(8)

from the Chuev model, the Langevin function, and the high-T behavior described by our eq.(8). The large temperature scale has not a physical sense, and this choice is only to show the high-T asymptotic behavior. We can see that the model presented in [1] predicts erroneously that the high-T magnetization is not null. Note also that the Langevin function describes correctly the expected behavior in the high-T limit and the correction of the anisotropy is very small (falling as $1/T^5$).

We want to return to our previous affirmation, in the low-T regime discussion, that the Langevin curve does not describes the thermal equilibrium magnetization. This is evident for the high-T regime in eq.(8), although the correction is very small. Unfortunately, we can't make the same treatment in the deduction of eq.(8). However we can consider the low anisotropy ($K \to 0$) and low-T ($x \to \infty$) limits. In this case, the equilibrium normalized magnetization obtained from eq.(6), after performing the angular anisotropy average (eq.(11) in [1]) results:

$$\left\langle \frac{\mu}{\mu_0} \right\rangle \approx 1 - \frac{1}{x} - \frac{4\,K^2}{15\,(\mu\,H)^2}. \qquad (10)$$

In this expression we see that the anisotropy correction appears as -K^2, like in the high-T limit (eq.(8)). The low anisotropy contribution is important, and it is expected that in the strong anisotropy case it can not be negligible.

In conclusion we have shown that the model presented in [1] is not correct on the high-T limit because it is inconsistent with basic Statistical Mechanics arguments. In addition, the incorrect low temperature implementation led Chuev to conceptual errors. In despite of the above, we believe that the model introduced in [1] could be accurate on a low temperature limit (K, $\mu_0 H \gg k_B T$) and a careful implementation, considering plausible physical conditions, can describe systems in which the anisotropy dominates.

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