Scaling form for zero-field cooled and field cooled susceptibility of superparamagnet

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A scaling form of the zero-field cooled (ZFC) and field-cooled (FC) magnetic susceptibility is presented for superparamagnets based on the the Néel model. Numerical calculation is carried out by using the Matrhematica 5.0. Recently we find that stage-2 $Cu_{0.93}Co_{0.07}Cl_2$ graphite intercalation compound (GIC) provides a model system of superparamagnets. An extensive study on the superparamagnetism of this system is reported in a paper submitted to Phys. Rev. B (January, 2005).

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I. NÉEL MODEL

Superparamagnetism is a phenomenon by which the system may exhibit a behavior similar to paramagnetism at temperatures below the Curie or the Néel temperature. Superparamagnetism occurs when the system is composed of very small crystallites (1-10 nm). The energy required to change the direction of magnetization of a crystallite is called the crystalline anisotropy energy and depends both on the material properties and the crystallite size. As the crystallite size decreases, so does the crystalline anisotropy energy, resulting in a decrease in the temperature at which the material becomes superparamagnetic.

In the Néel model,[1] the particles exhibit single-domain ferromagnetic behavior below the blocking temperature T_b, and are superparamagnetic above T_b. In the superparamagnetic state, the moment of each particle freely rotates, so a collection of particles acts like a paramagnet where the constituent moments are ferromagnetic particles (rather than atomic moments as in a normal paramagnet).

We consider a single-domain particle with uniaxial anisotropy. The variable part of the energy is then given by an expression of the type

$$F = \Delta E_a \sin^2\theta$$

where $\Delta\ E_a = K_u V$, θ is an angle between the magnetization and the easy direction. Either $\theta = 0$ or π is a direction of minimum energy. These directions are separated by an energy barrier of the height ΔE_a. The magnetization will remain stable and lie along these directions unless some perturbing force exists that can take the magnetization over the energy barrier. Thermal agitation may provide such a perturbation. This process is most likely to occur if the volume V of the particle is small, so that the height of the energy barrier is lowered, or if the temperature T is high. If the process does occur, the time average of the remanence will be zero. Particles whose magnetization changes spontaneously are analogous to paramagnetic atom, except that their magnetic moment is much larger. Such particles are said to exhibit superparamagnetism. Their existence was first predicted by Néel.

In the Néel relaxation process, the relaxation time of the magnetization between these two states is given by thermal activation (Arrehenius law),

$$\tau = \tau_0 \exp\left(\frac{\Delta E_a}{k_B T}\right), \tag{1}$$

where τ_0 is a microscopic limiting relaxation time (usually $\tau_0 \approx 10^{-9}$ sec), k_B is the Boltzmann constant, and ΔE_a is the height of the energy barrier due to anisotropy. The energy barrier in the presence of an DC magnetic field H is given by

$$\Delta E_a = K_u V \left(1 - \frac{H}{H_K}\right)^2, \tag{2}$$

where K_u is the uniaxial anisotropy constant, V is the particle volume, H_K is the anisotropy field defined by $H_K = 2K_u/M_s$, and M_s is the saturation magnetization of the particle. Note that the energy barrier ΔE_a is proportional to V. In other words, the relaxation time becomes large in the limit of large V. The particles are assumed to be noninteracting and the blocking temperature is given by

$$T_b(H) = \frac{K_u V}{k_B \ln(\tau_m/\tau_0)} \left(1 - \frac{H}{H_K}\right)^2, \tag{3}$$

or

$$\frac{T_b(H)}{T_b(H=0)} = \left(1 - \frac{H}{H_K}\right)^2,$$

where τ_m is the measurement time. The measurement time is t_m typically 1-100 sec for DC measurements and is the inverse of the measurement frequency for the AC measurements. When we have typically $\tau_0 = 10^{-9}$ sec and $\tau_m = 10^2$ sec, τ_m is estimated as

$$\tau_m = \tau_0 \exp\left(\frac{\Delta E_a}{k_B T_b}\right),$$

or

$$\frac{\Delta E_a}{k_B T_b} = \ln\left(\frac{\tau_m}{\tau_0}\right) = \ln(10^{11}) = 25.328,$$

leading to $\Delta E_a = 25.328 k_B T_b \approx 25 k_B T_b$. Below the blocking temperature T_b of the order $E_a/25k_B$, the fluctuations between the two states are becoming long enough to be observable on a laboratory time scale.

II. FERROMAGNETIC BLOCKED STATE

For $V < V_p$, the particle moment can achieve thermal equilibrium in the time of measurement and exhibits superparamagnetic behavior, while for $V > V_p$ the particle moment is blocked. Superparamagnetism in such clusters is frozen into a more stable ferromagnetic state at $T = T_b$. The particle moment is blocked in the direction of the easy axis. In a single domain particle the easy directions of magnetization are separated by ΔE_a. If the particle size is sufficiently small, above T_b thermal fluctuations dominate and particles can spontaneously switch its magnetization from one easy axis to another. Such a system of superparamagnetic particles does not show hysteresis in the M-H curves above T_b; hence H_c and M_R are zero. Moreover, the magnetization curves measured above T_b are expected to superimpose on each other when plotted as a function of H/T.

Above T_b, if all particles have the same volume V, the magnetization M^{sp} of superparamagnetic particles is given by[2]

$$M^{sp}_{ZFC}(V) = M^{sp}_{FC}(V) = \epsilon M_s L\left(\frac{M_s V H}{k_B T}\right), \quad (4)$$

where ϵ is the volume fraction occupied by ferromagnetic particles. In general, the magnetization of the superparamagnetism is considerably larger than that of atomic paramagnetism, and shows a tendency to saturate in rather small magnetic fields. Note that $L(x)$ ia a Langevin function defined by

$$L(x) = \coth(x) - 1/x.$$

This function $L(x)$ can be expanded in the vicinity of $x = 0$ as

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \frac{2x^5}{945} - \frac{x^7}{4725} + \frac{2x^9}{93555} - \frac{1382x^{11}}{638512875} + \cdots.$$

In the limit of $x \to \infty$, $L(x)$ reaches 1. When the system is in a blocked state below T_b, the magnetization of the ferromagnetic block state, $M^{bl}_{ZFC}(V)$ is given by[2]

$$M^{bl}_{ZFC}(V) = \frac{\epsilon M_s^2 H}{2K_u}\left\langle \sin^2\phi \right\rangle = \frac{\epsilon M_s^2 H}{3K_u},$$

noting that

$$\left\langle \sin^2\phi \right\rangle = \frac{1}{4\pi}\int_0^{\pi} \sin^2\phi(2\pi\sin\phi)d\phi = \frac{2}{3},$$

where ϕ is the angle between the applied field and the easy direction of the magnetization and the average is over all particles. The ZFC and FC

$$M^{bl}_{ZFC}(V) = \frac{\epsilon M_s^2 H}{3K_u}, M^{bl}_{FC}(V) = \epsilon M_s L\left(\frac{M_s V H}{k_B T_b}\right) \quad (5)$$

in a blocked state below T_b.

III. SCALING FORM OF THE ZFC AND FC SUSCEPTIBILITY

In summary, we have expressions for the ZFC and FC susceptibility given by by

$$\begin{aligned} M^{sp}_{ZFC} &= M^{sp}_{FC} = \epsilon M_s L\left(\frac{M_s V H}{k_B T}\right) = \epsilon M_s L\left(\frac{2hx}{y}\right), \\ M^{bl}_{ZFC} &= \frac{\epsilon M_s^2 H}{3K_u} = \epsilon M_s \frac{2h}{3}, \\ M^{bl}_{FC} &= \epsilon M_s L\left(\frac{M_s V H}{k_B T_b}\right) = \epsilon M_s L\left(2h\frac{\ln(\tau_m/\tau_0)}{(1-h)^2}\right), \end{aligned}$$

where h $(= H/H_K)$ is a magnetic field normalized by H_K $(= 2K_u/M_s)$, y $(= k_B T/(K_u\langle V\rangle))$ is the reduced temperature, x $(= V/\langle V\rangle)$ is the volume ratio, and x_m is defined by

$$x_m = \frac{V_m}{\langle V\rangle} = \frac{k_B T\ln(\tau_m/\tau_0)}{K_u\langle V\rangle} = y\frac{\ln(\tau_m/\tau_0)}{(1-h)^2}.$$

Thus we have

$$\begin{aligned} \frac{M_{ZFC}(T,H,x)}{H} &= [\frac{M^{sp}_{ZFC}}{H}U_{-1}(x_m - x) \\ &\quad + \frac{M^{bl}_{ZFC}}{H}U_{-1}(x - x_m)]f(x) \\ &= \frac{\chi_0}{h}[L\left(\frac{2hx}{y}\right)U_{-1}(x_m - x) \\ &\quad + \frac{2}{3}hU_{-1}(x - x_m)]f(x), \end{aligned} \quad (6)$$

and

$$\begin{aligned} \frac{M_{FC}(T,H,x)}{H} &= [\frac{M^{sp}_{FC}(x)}{H}U_{-1}(x_m - x) \\ &\quad + \frac{M^{bl}_{FC}(x)}{H}U_{-1}(x - x_m)]f(x) \\ &= \frac{\chi_0}{h}[L\left(\frac{2hx}{y}\right)U_{-1}(x_m - x) \\ &\quad + L\left(2h\frac{\ln(\tau_m/\tau_0)}{(1-h)^2}\right)U_{-1}(x - x_m)]f(x), \end{aligned} \quad (7)$$

where χ_0 $[= \epsilon M_s/HK = \epsilon M_s^2/(2K_u)]$ is a constant susceptibility, $U_{-1}(x)$ is the step function ($U_{-1}(x) = 1$ for $x \geq 0$ and 0 for $x < 0$), and $f(x)$ is assumed to be a log-normal distribution function

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma x}\exp\left[-\frac{(\ln x)^2}{2\sigma^2}\right].$$

Then the total ZFC and FC susceptibility are given by

$$\chi_{ZFC}(T,H) = \frac{1}{H}\int_0^{\infty} M_{ZFC}(T,H,x)dx,$$

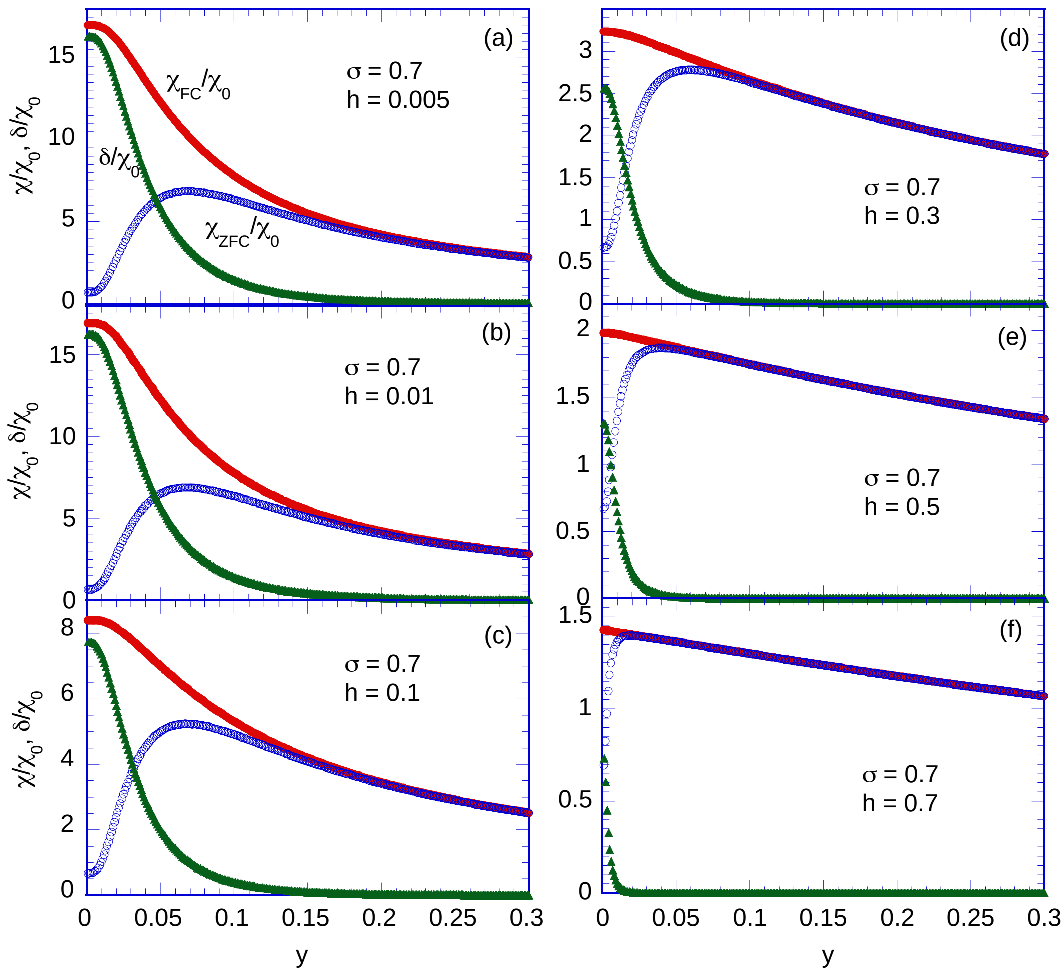

FIG. 1: Plot of χ_{ZFC}/χ_0, χ_{FC}/χ_0, and $\delta = (\chi_{FC} - \chi_{ZFC})/\chi_0$ as a function of reduced temperature y, where σ is fixed as $\sigma = 0.7$ and $h = H/H_K$ is changed as parameters.[3] $\ln(\tau_m/\tau_0) = 25.328$.

and

$$\chi_{FC}(T,H) = \frac{1}{H}\int_0^\infty M_{FC}(T,H,x)dx.$$

Using the scaling form of $M_{ZFC}(T,H,x)$ and $M_{ZFC}(T,H,x)$, the ZFC and FC susceptibility are given by the final forms;

$$\frac{\chi_{ZFC}}{\chi_0} = \frac{1}{h}\int_0^\infty [L\left(\frac{2hx}{y}\right)U_{-1}(x_m - x) + \frac{2}{3}hU_{-1}(x - x_m)]f(x)dx, \quad (8)$$

$$\frac{\chi_{FC}}{\chi_0} = \frac{1}{h}\int_0^\infty [L\left(\frac{2hx}{y}\right)U_{-1}(x_m - x) + L\left(2h\frac{\ln(\tau_m/\tau_0)}{(1-h)^2}\right)U_{-1}(x - x_m)]f(x)dx. \quad (9)$$

IV. RESULT OF NUMERICAL CALCULATION

Figure 1 shows a typical example of χ_{ZFC}/χ_0, χ_{FC}/χ_0, and the difference defined by $\delta = (\chi_{ZFC} - \chi_{FC})/\chi_0$, as a function of the normalized temperature y $(= k_BT/(K_u\langle V\rangle)$, by the appropriate choice of two parameters;[3]
(1) $h = H/H_K$: the normalized magnetic field,
(2) σ: width of the log-normal distribution function.
Note that $\ln(\tau_m/\tau_0) = 25.328$ is used here, $x = V/\langle V\rangle$ is an integration variable, and the value of x_m is a function of y, h, and t_w/t_0; $x_m = \langle V\rangle/V_m = y\ln(t_m/\tau_0)/(1-h)^2$.

APPENDIX:

Mathematica 5.0 program for the calculation of ZFC and FC susceptibility.

Because of the use of numerical integration, one may find some warning messages concerning the divergence. In spite of this, one can find reasonable results such as

Fig. 1.

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