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A Review on The Effect of Particle Size Distributions on The Entropy

Mr. Ali O. A keelani Student, Ph.D Researcher, Aligarh Muslim University. Prof.Ibrahim Abu-Aljarayesh Professor, Yarmouk University. Assit.Prof.Dr.Shahid Husain Assistant Professor, Aligarh Muslim University.

Abstract:

This paper presents the effects of different particle size distribution functions on the magnetic entropy change ΔS for fine magnetic particle systems within the context of super paramagnetic theory. The model is taken of superparamagnetic fine particle with particle size distribution in magnetic media. Finally the method used in numerical calculations of the entropy change is presented on ideal superparamagnetic particles without interaction, then general superparamagnetic behavior of an aligned assembly of uni axially anisotropic particles, and then the effect of magnetic dipolar interaction is considered, finally the effect of both magnetic dipolar interaction an anisotropy constant is considered.

Index Terms:

Fine Magnetic particles, paramagnetism, magnetic anisotropy

I. Introduction:

The effects of different particle size distribution functions on the magnetic entropy change ΔS for fine magnetic particle systems within the context of superparamagnetic theory. The magnetic entropy change ΔS in magnetic fine particle system were calculated numerically as a function of mean volume

of particles (V), the standard deviation(σ), and the magnetic field(H), the absolute temperature(T), using the classical theory of super paramagnetism. Frenkel and Dorfman were the first to predict that a particle of ferromagnetic material, below a critical particle size, would consist of a single magnetic domain. Kittel and others have estimated this critical particle size, and an approximate figure for a spherical

sample of the common ferromagnetic materials Fe_3O_4 is a radius of 150Å. Consider an assembly of uniaxial, single-domain particles, each with an anisotropy energy $E = KV \sin^2 \theta$, where K is the anisotropy constant and θ is the angel between the magnetic moment μ of the dipole and the applied field (or the easy axis). If the volume of each particle is V, then the energy barrier that must be overcome before a particle can reverse it is magnetization is $\Delta E = KV$. Now in any material, fluctuations of thermal energy are continually occurring on a microscopic scale. In 1949 Néel pointed out that, if single-domain particles became small enough, KV would become so small that energy fluctuations could overcome the anisotropy forces and spontaneously reverse the magnetization of a particle from one easy direction to the other, even in the absence of an applied field. Each particle has a magnetic moment $\mu = \mu_0 M_S V$ and, if a field is applied, the field will tend to align the moments of the particles, whereas thermal energy will tend to disalign them. This is just like the behavior of a normal paramagnetic, with one notable exception. The magnetic moment per atom or ion in a normal paramagnetic is only a few Bohr magnetons, whereas a spherical particle of iron, say, 50 Å in diameter, contains 5560 atoms and has the relatively enormous moment of $12,000 \,\mu_B$.

As a result, Bean has coined the term `super paramagnetism` to describe the magnetic behavior of such particles. If K = 0, so that each particle in the assembly has no anisotropy, then the moment of each particle can point in any direction, and the classical theory of paramagnetism will be applied, then the energy of each particle is given by:

$$E = -\mu H \cos \theta$$

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Then the total magnetization of the assembly consisting of magnetic particles, will be given by:

$$M = M_{sb}L(\alpha)$$

Here M_{sb} is the saturation magnetization of the assembly. $\alpha = \frac{\mu H}{K_B T}$ and $L(\alpha)$ is called Langevin

function, and is given by:

$$L(\alpha) = coth\alpha - \frac{l}{\alpha}$$

So this treatment of the thermal equilibrium magnetization properties of an assembly of isotropic single domain particles, of course, analogous to the Langevin treatment of atomic paramagnetism It differs only in that the moment μ we are dealing with is not that of a single atom, but rather of a single domain ferromagnetic particle. Which may contain more than 10^5 atoms ferromagnetically coupled by exchange forces large susceptibilities are involved. At the other extreme, if K is finite and the particles are aligned with their easy axes parallel to one another and to the field, then the moment directions are severely quantized, either parallel or anti parallel to the field, and quantum theory will apply. Then the total magnetization is given by:

$$M = M_{sb} \tanh \alpha$$

Two aspects of superparamagnetic behavior are always true:

- 1. Magnetization curves measured at different temperatures superimpose when M is plotted as a function of H/T.
- 2. There is no hysteresis, we are therefore dealing with particles having diameters smaller than the critical value.

Superparamagnetic materials consist of individual domains of elements that have ferromagnetic properties in bulk. Their magnetic susceptibility is between that of ferromagnetic and paramagnetic materials. Examples of a superparamagnetic material include iron containing contrast agents for bowel, liver, and lymph node imaging. The magnetic entropy change ΔS in magnetic fine particle system were calculated numerically as a function of mean volume

of particles (V), the standard deviation (σ), and the magnetic field (H), the absolute temperature (T). using the classical theory of superparamagnetism. Frenkel and Dorfman were the first to predict that a particle of ferromagnetic material, below a critical particle size, would consist of a single magnetic domain. Kittel and others have estimated this critical particle size, and an approximate figure for a spherical sample of the common ferromagnetic materials Fe_3O_4 is a radius of 150Å. Consider an assembly of uniaxial, single-domain particles, each with an anisotropy energy $E = KV \sin^2 \theta$, where K is the anisotropy constant and θ is the angel between the magnetic moment μ of the dipole and the applied field (or the easy axis). If the volume of each particle is V, then the energy barrier that must be overcome before a particle can reverse it is magnetization is $\Delta E = KV$. Now in any material, fluctuations of thermal energy are continually occurring on a microscopic scale. In 1949 Néel pointed out that, if single-domain particles became small enough, KV would become so small that energy fluctuations could overcome the anisotropy forces and spontaneously reverse the magnetization of a particle from one easy direction to the other, even in the absence of an applied field. Each particle has a magnetic moment $\mu = \mu_0 M_S V$ and, if a field is applied, the field will tend to align the moments of the particles, whereas thermal energy will tend to disalign them. This is just like the behavior of a normal paramagnetic, with one notable exception. The magnetic moment per atom or ion in a normal paramagnetic is only a few Bohr magnetons, whereas a spherical particle of iron, say, $50\,\text{\AA}$ in diameter, contains 5560 atoms and has the relatively enormous moment of $12,000 \mu_B$.

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II. Related Theory:

The theory deals with the mathematical derivation of the change in the entropy ΔS of fine magnetic particle systems, taking into account the effect of particles size distributions. The organization is devoted to give a theoretical background for the evaluation of the free energy for a paramagnetic system, magnetic and magnetocaloric properties of superparamagnetic systems utilizing first the thermodynamical approach, then the statistical approach.

1. Evaluation of Free Energy for a Paramagnetic System:

Paramagnetism describes a feeble magnetism which exhibits positive susceptibility of the order of $\chi=10^{-5}$ - 10^{-2} [18-22]. This magnetic behavior is found in materials that contain magnetic atoms or ions that are widely separated so that they exhibit no appreciable interaction with one another. Paramagnetic materials include oxygen and ions of various metals like Fe, Mg, and Gd. These ions have unpaired electrons, resulting in a positive magnetic susceptibility. The magnitude of this susceptibility is less than one thousands of that of ferromagnetic materials. Theory of paramagnetism assumes that the discrete sources of magnetic moments do not interact with one another, thus the thermal energy causes them to fluctuate among all possible orientations without preference, and unless an external magnetic field H is applied the magnetization of the material as a whole is zero [23]. However, at any temperature T, application of an external magnetic field H produces a preferential orientation of the moments, resulting in a magnetization M which, with increasing H, rises at first linearly and then more slowly as it approaches a saturation value corresponding to a complete alignment of all the moments parallel to the field H. Moreover, the effects of H and T on the moment's alignment oppose each other in such away that M depends universally on the ratio of H/T. However, according to the classical theory, the magnetic moments are assumed to be freely rotating. Thus, for a substance containing n-magnetic moments μ per unit volume, the magnetization M can be calculated using standard statistical physics procedure.As a model of a Hence we must calculate the partition function of a system with the energy:

 $E = -\sum_{i=1}^{N} \mu_i \cdot H$ If the uniform field H points in the z-direction, then the orientation of each dipole can be expressed by the polar angles \mathcal{G}_i and ϕ_i . Each microstate corresponds exactly to a set $\{\mathcal{G}_i, \phi_i\}$ of orientations of all dipoles. The partition function over all microstate depends on *T*, *H*, and *N*, where the magnetic field plays a role similar to that which the volume usually plays:

$$Z(T,H,N) = \int d\Omega_1 \int d\Omega_2. \quad . \quad \int d\Omega_N \exp\left\{\frac{\mu H}{kT} \sum_{i=1}^N \cos \theta_i\right\}$$

 $\xrightarrow{\rightarrow} \rightarrow$ Where $\mu_i \cdot H = \mu_{Zi} H_Z = \mu H \cos g_i$ is assumed. The integrals $\int \Omega_i$ extend over all spatial angles.

The partition function factors, since we have not assumed any interaction between the individual dipoles:



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$$Z(T,H,N) = \left[Z(T,H,1)\right]^N$$

$$Z(T,H,I) = \int d\Omega \exp\left\{\frac{\mu H}{kT}\cos\vartheta\right\}$$

The above integral is standard and has a value of;

$$Z(T,H,1) = 4\pi \frac{\sinh\left(\frac{\mu H}{kT}\right)}{\frac{\mu H}{kT}}$$

The free energy for this system can be obtained from the following relation:

$$F(T,H,N) = -kT \ln Z(T,H,N)$$

And the magnetic entropy (S) can be obtained from the equation of state, i.e.

$$S = -\left(\frac{\partial F}{\partial T}\right)_{H}$$

$$S = Nk \left[ln(4\pi) + ln(\frac{sinh(\frac{\mu H}{kT})}{\frac{\mu H}{kT}}) + 1 - \frac{\mu H}{kT} coth(\frac{\mu H}{kT}) \right]$$
The

change in entropy of a magnetic system can be also calculated using standard classical thermodynamics. Where T and H are respectively the temperature and applied magnetic field. From this exact differential, the following Maxwell relation may be derived relating the incremental entropy change accompanying an incremental change in magnetic field to the measurable quantities of magnetization and temperature:

$$\left(\frac{\partial S}{\partial H}\right)_{T} = \left(\frac{\partial M}{\partial T}\right)_{H}$$

Upon integrating over H, the total entropy change of the system upon the application of a magnetic field may be determined:

$$\Delta S = \int_{0}^{H} \left(\frac{\partial M}{\partial T}\right)_{H} dH$$

2. Magnetocaloric Effect:

The magnetocaloric effect is the adiabatic temperature change of a material upon application of a magnetic field. it is very closely related to the isothermal field induced entropy change, which, for temperature changes, differs from the magnetocaloric effect by a factor of the temperature, divided by the specific heat of the material. By grouping spins together in superparamagnetic clusters, the magnetic moments are more easily aligned than in paramagnetic systems, and for certain range of field, temperature and cluster size, the entropy of the spins is more easily changed by the application of a field.

Certain magnetic materials heat up when they are placed in a magnetic field and cool down when the field is moved away. This phenomenon is known as the magnetocaloric effect. For a given material, the larger the change in magnetic field, the larger the magnetocaloric effect. Pierre Weiss and A.Picard [33] first explained this principle in 1918. In 1926 P.Debye and W.Giaque [33], suggested how the step magnetic refrigeration cycles could be used to reduce the temperatures of some research samples from **1** K to a 2000 ll fraction of a Kelvin. Giauque and MacDougall experimentally verified the method in 1933.

III. Related Work:(I) Superparamagnetism System:

The magnetic entropy of N-independent magnetic moments placed in a uniform field H, at temperature T, is calculated directly through the partition function Z, assuming classical behavior of the moments, from

$$S_{C} = Nk \left[ln(4\pi) + ln(\frac{sinh(\frac{\mu H}{kT})}{\frac{\mu H}{kT}}) + 1 - \frac{\mu H}{kT} coth(\frac{\mu H}{kT}) \right]$$

This expression for the entropy of the magnetic moments has a value of $Nk \ln(4\pi)$ at H = 0, high field limit (μ H>>kT) i.e.;

$$S_c \approx Nk \left[ln(4\pi) + 1 - ln(\frac{2\mu H}{kT}) \right]$$



Which become negative for large H and low T. This anomaly is due to the classical nature of the system and is related to the fact that in a classical system there is no minimum energy as in a quantum system.

$$= Nk \left[1 + ln(\frac{sinh(\frac{mH}{kT})}{\frac{\mu H}{kT}}) - \frac{\mu H}{kT} coth(\frac{\mu H}{kT}) \right]$$

We can find ΔS_{max} by setting $\frac{\partial \Delta S}{\partial \alpha} = 0$, where

 $\alpha = \frac{mH}{kT}$, then a transidental equation results, namely:



$$\alpha = \frac{\mu H}{kT}$$
$$\alpha^2 \csc h^2 \alpha - 2 + \alpha \coth \alpha + \ln(\frac{\sinh \alpha}{\alpha}) = 0$$

Fig 2.1 Shows the entropy changes $-\Delta S \ Vs \ \alpha \text{ of a}$ superparamagnet with saturation moment μ_{sb} as a function of particle moment μ , induced by removal of a field H=5000Oe at a temperature T=300 K. For a given value of H and T, the maximum entropy change occurs at $\alpha = 3.5$ where T ΔS =-0.272 μ_0 H.Thus, ΔS_{max} can be found numerically. ΔS has a maximum change at $\alpha \approx 3.5$ (Fig 2.1) and it's value is [10,17,33,34]:

$$\Delta S_{max} = -0.272 \frac{M_{sb}H}{T}$$

The broadness of the maximum in Eq shows that the entropy change for superparamagnetic particles drops off slowly as particle sizes deviate from optimum. The decrease in ΔS is due to decreasing the number of clusters as the cluster size grows.Note that in this limit ΔS increases linearly with μ when the saturation magnetization M_{sb} is held constant. For paramagnets with magnetic moments consisting of single atoms, Eq (2-15) is a good approximation except for very low temperatures and very high fields, where saturation effects can be seen. In the low field limit, the entropy change is proportional to $\frac{H^2}{T^2}$, in contrast, in a

superparamagnetic material where saturation effects will occur at higher temperatures and low fields, that ΔS in the optimized superparamagnetic material is proportional to $\frac{H}{T}$.

(ii) The effect of magnetic anisotropy (uniaxially anisotropic particles):

The magnetic energy of such particles with uniaxial anisotropy is usually written in the form;

$$E_K = KV \sin^2 \vartheta$$

where \mathcal{G} is the angle between the magnetization direction and an easy direction of magnetization, V is the particle volume, and K is the anisotropy energy per unit volume. For very small particles, the energy barrier KV, which separates the two minima at

 $\mathcal{G} = 0^{\circ}$ and $\mathcal{G} = 180^{\circ}$, may be smaller than the thermal energy, even below room temperature. This results in superparamagnetic relaxation, i.e. spontaneous fluctuations of the magnetisation direction. The superparamagnetic relaxation time (τ) is given by:

$$\tau = \tau_{\circ} exp(\frac{KV}{kT})$$

Where τ_{\circ} is of the order of $10^{-10} - 10^{-13}$ s.



Consider an assembly of particles, each having a uniaxial symmetry i.e., $E_K = KV \sin^2 \vartheta$, if a field **H** is applied along the symmetry axis. This will lead to a different Boltzman distribution of orientations of μ with respect to **H** in thermal equilibrium than we had without the anisotropy term. The magnetisation curve will no longer be a simple Langevin function. The partition function which describes the thermal equilibrium behavior of an aligned assembly of uniaxially anisotropic particles in a field **H** applied along the direction of alignment is:

$$Z(T,H,I) = 2\pi \int_{0}^{\pi} \sin \vartheta \exp(-\frac{E}{kT}) d\vartheta$$
$$= 2\pi \int_{0}^{\pi} \sin \vartheta \exp(-(\alpha \cos \vartheta - \beta \sin^{2} \vartheta)) d\vartheta$$

where $\alpha = \frac{\mu H}{kT}$, $\beta = \frac{KV}{kT}$, and ϑ is the angle between the spontaneous magnetization and the anisotropy axis of particle of volume V.

From Eq.2.23 Z is given with Precision of α^2 by [10]:

$$Z = 4\pi A \left\{ 1 + \frac{\alpha^2}{2} [\cos^2 9_0 \frac{B}{A} + \frac{1}{2} \sin^2 9_0 (1 - \frac{B}{A})] \right\}$$

Where

_

$$A = \int_{0}^{t} e^{\beta t^{2}} dt \text{ and } B = \int_{0}^{t} e^{-\beta t^{2}} dt$$

If the diameter is less than 80Å then $\beta < 1$, so we can expand Eq(2-21) as:

$$exp(-\beta_{sin}^2 \mathcal{G}) = 1 - \beta_{sin}^2 \mathcal{G} + \dots$$

Then Z reduces to:

$$Z = 4\pi [\sinh\alpha(\frac{1}{\alpha} + \frac{2\beta}{\alpha^3}) - \frac{2\beta}{\alpha^2} \cosh\alpha]$$
 The

magnetic entropy S(H) of the system can then be found from the thermodynamic relation Eq(2-11), so we find:

$$S(H) = Nk[ln(4\pi\left\{\sinh\alpha(\frac{1}{\alpha} + \frac{2\beta}{\alpha^3}) - \frac{2\beta}{\alpha^2}\cosh\alpha\right\}) + 2$$
$$+ \frac{\sinh\alpha(2\beta - 1) - \alpha\cosh\alpha}{\sinh\alpha(1 + \frac{2\beta}{\alpha^2}) - \frac{2\beta}{\alpha}\cosh\alpha}$$

By increasing the field from θ to

H, the entropy changes by:

$$\Delta S = Nk \left[ln \left\{ sinh\alpha \left(\frac{1}{\alpha} + \frac{2\beta}{\alpha^3} \right) - \frac{2\beta}{\alpha^2} cosh\alpha \right\} + 2 - ln \left(1 - \frac{2}{3}\beta \right) \right]$$

+
$$\frac{sinh\alpha \left(2\beta - 1 \right) - \alpha cosh\alpha}{sinh\alpha \left(1 + \frac{2\beta}{\alpha^2} \right) - \frac{2\beta}{\alpha} cosh\alpha} - \frac{1}{\left(\frac{2}{3}\beta - 1 \right)} \right]$$

Which can be rewritten as Where μ_0 is the permeability of vacuum

$$(\mu_0 = 4\pi \times 10^{-7} H m^{-1})$$
, and \mathcal{E} is the concentration of magnetic particles

concentration of magnetic particles.

(iii) The effect of magnetic dipolar interactions:

Magnetic dipolar interaction (MDI) is always present in an assembly of ferromagnetic (or antiferromagnetic) particles. For close compact assembly, with particles very near to each other. The MDI energy is around $5\times10^6 \ erg/cm^3$ for metallic iron (but the MDI anisotropic part can be much smaller, and the MDI energy value is lower because of spin disorder occurring in particle surface), to be compared to the magnetocrystalline anisotropy value which is equal to $5.10^5 \ erg/cm^3$ [35]. In the case of oxidize iron MDI energy is around 3.10^4 and $10^3 \ erg/cm^3$ for a diameter *D* equal to 30 and 100Å, respectively.

In order to treat the MDI effects, we can distinguish two cases (i) a regular arrangement of identical particles, and (ii) a disordered assembly of nonidentical particles with a certain volume distribution.



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In the first case, the particles are indistinguishable and their μ sees the same energy barrier.

A synchronous rotation of μ is expected. In the second case, E_B is distributed, depending on the volume and on MDI. This results in a distribution of the relaxation times. In such case, it is not possible to calculate MDI as in static condition because the angle between μ of two non-identical particles fluctuate with time. We remark that very small variations in the particle volume induce such an effect, which shows that the first case must never be considered for real samples. The model for mean MDI energy E_{int} is

given by $E_{int} = -E_{Bint} \cos^2 \vartheta$

$$E_{Bint} = \mu^2 V_i \sum_j b_{ij} L(\frac{\mu^2 V_i a_{ij} \cos g_i}{kT})$$

 $E_{Bint} = \left(\frac{\mu^2}{V}\right) \sum_{j} b_j L\left(\frac{\mu^2 a_j}{VkT}\right) \text{ Where } L \text{ denotes}$

the langevin function, V is the mean volume,

$$a_j = V \frac{(3\cos 2\alpha_j - 1)}{d_j^3}$$
 and b_j close to a_j . Her

 d_j and a_j correspond respectively to the distance and to an angle parameter of space position of the particle j, with respect to an origin particle, for regular arrangement of particles with uniform volume V. Eq(2-33) can be rewritten as:

$$E_{Bint} = M^2 V_i \sum_{j} b_{ij} L(\frac{M^2 V_i a_{ij} \cos \theta_i}{kT})$$

The E_{Bint} value can be simplified through the approximation of the langevin function: $L(x) = \frac{x}{3}$

for x < 0.9 and $L(x) = 1 - \frac{1}{x}$ for x < 2, if the

first approximation is fulfilled for the first neighbors, it will also be valid for other neighbors, in this case E_{Bint} is approximated by [35]:

$$E_{Bint} = \left(\frac{6}{kT}\right) \frac{\mu^4}{d^6} \qquad for \quad kT > 1.1 \frac{\mu^2}{d^3}$$

Nevertheless, this approximation is valid for temperatures relatively high. The energy of the particle will be:

$$E = -E_{Bint}\cos^2 \vartheta - \mu H\cos \vartheta$$

The partition function, which describes the thermal equilibrium behavior of an aligned assembly with dipolar interaction, can be written as:

$$S(0) = Nk [ln(4\pi(1+\frac{1}{3}\lambda)) - \frac{\lambda}{(3+\lambda)}]$$
$$Z = 2\pi \int_{0}^{\pi} sin \, \vartheta exp(-\frac{E}{kT}) d\vartheta$$

Where $\alpha = \frac{\mu H}{kT}$, $\lambda = \frac{E_{Bint}}{kT}$, since $\lambda < 1$, so we can expand

 $exp(\lambda_{cos}^2 \mathcal{G}) = 1 + \lambda_{cos}^2 \mathcal{G} + .$. Equation reduces to:

$$Z = 2\pi \int_{0}^{\pi} \sin \theta (1 + \lambda \sin^{2} \theta) \exp(\alpha \cos \theta) d\theta$$

Which yields;

$$Z = 4\pi [\sinh\alpha(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3}) - \frac{2\lambda}{\alpha^2} \cosh\alpha]$$

The magnetic entropy S(H) of the system can then be found from the thermodynamical relations as in, so we find:

$$S(H) = Nk \left[ln \left(4\pi \left\{ sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha \right\} \right) \right] As + \frac{\left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) \frac{sinh\alpha - \alpha cosh\alpha}{\alpha}}{sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha}$$
$$H \rightarrow 0 \quad S(H) \text{ has a value of:}$$



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By increasing the field from 0 to H, the entropy changes ΔS is given by:

$$\Delta S = \frac{\epsilon k}{V \mu_0} \left[ln \left\{ sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha \right\} - ln(1 + \frac{1}{3}\lambda) \right] \\ + \frac{\left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) \frac{sinh\alpha - \alpha cosh\alpha}{\alpha}}{sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha} + \frac{\lambda}{(3 + \lambda)} \right] \\ \Delta S = Nk \left[ln \left\{ sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha} \right\} - ln(1 + \frac{1}{3}\lambda) + \frac{\left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) \frac{sinh\alpha - \alpha cosh\alpha}{\alpha}}{sinh\alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3} \right) - \frac{2\lambda}{\alpha^2} cosh\alpha} + \frac{\lambda}{(3 + \lambda)} \right]$$

(iv) The effect of both magnetic dipolar interactions and anisotropy energies:

The energy of the particle which describe the system will be

$$E = -E_{Bint}\cos^2 \vartheta - \mu H\cos \vartheta + KV\sin^2 \vartheta$$

The partition function, which describes the thermal equilibrium behavior of an aligned assembly with dipolar interaction with behavior of an aligned assembly of uniaxially anisotropic particles, can be written as:

$$Z = 2\pi \int_{0}^{\pi} \sin \vartheta \exp(-\frac{E}{kT}) d\vartheta$$
$$= 2\pi \int_{0}^{\pi} \sin \vartheta \exp(\alpha \cos \vartheta + \lambda \cos^{2} \vartheta - \beta \sin^{2} \vartheta) d\vartheta$$

Simple manipulation Eq(2-48) reduces to:

$$Z = 2\pi \int_{0}^{\pi} \sin \theta (1 + \lambda \sin^{2} \theta - \beta \sin^{2} \theta) \exp(\alpha \cos \theta) d\theta$$

Straightforward evaluation of yields:

$$Z = 4\pi [\sinh\alpha(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3}) - \frac{2\lambda+2\beta}{\alpha^2} \cosh\alpha]$$

The magnetic entropy S(H) of the system can then be found from the thermodynamic relation in, so we find:

$$\begin{split} S(H) &= Nk \left[ln(4\pi \left\{ sinh\alpha(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3}) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha \right\} \right) \\ &+ 1 + \frac{(2\beta + \frac{2\beta}{\alpha^2}) \frac{sinh\alpha}{\alpha} - cosh\alpha[1+\lambda + \frac{2\beta}{\alpha^2}]}{sinh\alpha(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3}) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha} \right] \end{split}$$

When $H \rightarrow 0$ this expression for the entropy of the magnetic moments has a value of:

$$S(0) = Nk[ln(4\pi(1+\frac{1}{3}\lambda-\frac{2\beta}{3}))+\frac{2\beta-2\lambda}{(3+\lambda-2\beta)})]^{\text{By}}$$

increasing the field from 0 to H, the entropy changes ΔS is given by:

$$\Delta S = Nk \left[ln \left\{ sinh\alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3} \right) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha \right\} \right]$$

$$\frac{(2\beta + \frac{2\beta}{\alpha^2}) \frac{sinh\alpha}{\alpha} - cosh\alpha \left[1+\lambda + \frac{2\beta}{\alpha^2} \right]}{sinh\alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3} \right) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha} - ln \left(1 + \frac{1}{3}\lambda - \frac{2\beta}{3} \right) \right]$$

$$- \frac{2\beta-2\lambda}{(3+\lambda-2\beta)} + 1 \left[AS = \frac{sk}{\mu_0 V} \left[ln \left\{ sinh\alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3} \right) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha \right\} \right]$$

$$\frac{(2\beta + \frac{2\beta}{\alpha^2}) \frac{sinh\alpha}{\alpha} - cosh\alpha \left[1+\lambda + \frac{2\beta}{\alpha^2} \right]}{sinh\alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3} \right) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha} - ln \left(1 + \frac{1}{3}\lambda - \frac{2\beta}{3} \right)$$

$$- \frac{2\beta-2\lambda}{\alpha^3} - cosh\alpha \left[1+\lambda + \frac{2\beta}{\alpha^2} \right]}{sinh\alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^3} \right) - \frac{2\lambda+2\beta}{\alpha^2} cosh\alpha} - ln \left(1 + \frac{1}{3}\lambda - \frac{2\beta}{3} \right)$$

$$- \frac{2\beta-2\lambda}{(3+\lambda-2\beta)} + 1 \left[1 + \frac{1}{3}\lambda - \frac{2\beta}{3} \right]$$

In any real system there is bound to be a distribution of particle volume, which plays an important role in it is magnetic and magnetocaloric behavior.

For uniform size particles without interaction and spherically shaped we can derive ΔS as follow: Since S is an extensive quantity, the total entropy change is given by:

$$\Delta S_T = \Delta S_1 + \Delta S_2 + \Delta S_3. \quad . \quad . + \Delta S_N$$

 $= \sum_{i=1}^{N} \Delta S_i \text{ But for } N >> 1 \text{ we can replace the}$

summation by integration i.e.,



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Or equivalently;

$$\Delta S_T = \int_{V_{min}}^{V_{max}} \Delta S(V) F_i(V) dV$$

Thus, the ΔS as given by equations, were used, to evaluate ΔS_T , for superparamagnetic systems.

5. The different distribution functions for particle sizes used in this work:

The distribution functions for particle sizes are given by:

(a) Uniform distribution function (DD or UD) (Dirac):

 $F_{I}(V)dV = \delta(V - V)dV$

Where $F_{l}(V)dV$ defines the probability of a particle having a volume in the range V to V + dV, –

- V is the mean volume, V is the particle volume
- (b) Constant (Rectangular) distribution function (CD or RD):

$$F_2(V)dV = \frac{1}{V_{max} - V_{min}}dV \quad for \quad V_{max} \ge V \ge V_{min}$$

Where V_{max} and V_{min} are the maximum and minimum volume of particle respectively.

(c) Normal (Gaussian) distribution function (ND or GD):

$$F_{3}(V)dV = \frac{1}{\sigma\sqrt{2\pi}}exp - \frac{\left(V - V\right)^{2}}{2\sigma^{2}}dV$$

Where σ is the standard deviation.

(d) Log-Normal distribution function (LD):

$$F_4(V)dV = \frac{1}{\sigma V \sqrt{2\pi}} exp - \frac{\left(ln\frac{V}{-}\right)^2}{2\sigma^2} dV$$

Volume No: 3 (2016), Issue No: 2 (February) www.ijmetmr.com Where σ is the standard deviation of lnV.

Fig 2.2 Shows F(V) Vs the volume of particle V for CD, GD and LD distribution with a mean diameter of 80 Å, $\sigma_3=7\times10^{-26}$, $\sigma_4=0.6$, and a diameter range (20-200Å). Fig 2.3 Shows F(V) Vs V for the same distribution functions with a mean diameter of 50 Å, $\sigma_3=1\times10^{-26}$, $\sigma_4=0.1$, and a diameter range (20-80Å).



Fig 2.2 Shows F(V) Vs V for all distribution with a mean diameter of 80Å, $\sigma_3=7\times10^{-26}$, $\sigma_4=0.6$, and diameter range (20-200Å).





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Fig 2.3 Shows F(V) Vs V for all distributions with a mean diameter of 50 Å, $\sigma_3=1\times10^{-26}$, $\sigma_4=0.1$, and a diameter range (20-80Å).

2.5 Method of calculations:

The numerical calculations of the entropy change ΔS were performed using the MathCad computer package by the following procedure: First: the independent

 M_{sb} , V, K, and σ were introduced together with the values of the magnetic parameters for a system of Fe_3O_4 -fine particles. The moments are assumed for a non-interacting system and with (K=0). The values of H were varied between 500 and 8000 Oe in steps of 500 Oe, for T values ranging from 20 to 360K in steps of 20K. The values of V ranging from 2.5×10^{-27} to $40 \times 10^{-27} m^3$ in steps of $2.5 \times 10^{-27} m^3$. For noninteracting and spherically symmetric particles for Hvalues ranging from 500 to 8000 Oe in steps of 500 Oe, for T values ranging from 200 to 360K in steps of 10K, for K values ranging from 500 to 20000J/gm.K in J/gm.K.. But steps 500 for general of superparamagnetic system with magnetic dipolar interaction for H values ranging from 500 to 8000 Oe in steps of 500 Oe, for T values ranging from 20 to 360K in steps of 20K

The following expressions were used in the calculations:

For a non-interacting system:

From Equations ΔS_i is given by;

$$\Delta S_{i} = \frac{\mathcal{E}k}{\mu_{0}} \int_{V_{min}}^{V_{max}} \frac{1}{V} \left[1 + \ln(\frac{\sinh(\frac{mH}{kT})}{\frac{mH}{kT}}) - \frac{mH}{kT} \coth(\frac{mH}{kT}) \right] F_{i}(V) dV$$
For

superparamagnetic behavior with magnetic dipolar interactions:

From Equations ΔS_i is given by;

$$\Delta S_{i} = \frac{ek}{\mu_{0}} \int_{V_{min}}^{V_{max}} \frac{1}{V} \left[ln \left\{ sinh \, \alpha \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^{3}} \right) - \frac{2\lambda}{\alpha^{2}} cosh \, \alpha \right\} - ln \left(1 + \frac{1}{3} \lambda \right) + \frac{1}{2} \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha^{3}} + \frac{2\lambda}{\alpha^{3}} \right) - \frac{1}{2} \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha^{3}} + \frac{2\lambda}{\alpha^{3}} \right) - \frac{1}{2} \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{2} \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{2} \left(\frac{1}{\alpha} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{1}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{\lambda}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) - \frac{\lambda}{\alpha^{3}} \left(\frac{1}{\alpha^{3}} + \frac{\lambda}{\alpha^{3}} \right) \right)$$

$$\frac{\left(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3}\right)\frac{\sinh\alpha - \alpha\cosh\alpha}{\alpha}}{\sinh\alpha(\frac{1}{\alpha} + \frac{\lambda}{\alpha} + \frac{2\lambda}{\alpha^3}) - \frac{2\lambda}{\alpha^2}\cosh\alpha} + \frac{\lambda}{(3+\lambda)}JF_i(V)dV$$

For superparamagnetic behavior with uniaxial anisotropy and with magnetic dipolar interactions:

From equations ΔS_i is given by;

$$\Delta S_{i} = \frac{gk}{\mu_{0}} \frac{V \max}{V \min} \left[ln \left\{ \sinh \alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^{3}} \right) - \frac{2\lambda+2\beta}{\alpha^{2}} \cosh \alpha \right\} \right]$$

$$\frac{\left(2\beta + \frac{2\beta}{\alpha^{2}} \right) \frac{\sinh \alpha}{\alpha} - \cosh \alpha \left[1+\lambda + \frac{2\beta}{\alpha^{2}} \right]}{\sinh \alpha \left(\frac{1+\lambda}{\alpha} + \frac{2\lambda+2\beta}{\alpha^{3}} \right) - \frac{2\lambda+2\beta}{\alpha^{2}} \cosh \alpha} - \ln \left(1 + \frac{1}{3}\lambda - \frac{2\beta}{3} \right)$$

$$- \frac{2\beta-2\lambda}{\left(3+\lambda-2\beta\right)} + 1 \right] F_{i}(V) dV$$

Where $F_i(V)$ is given by Equations respectively.

IV CONCLUSION:

The presented paper provides the thesis work which deals with the effects of different particle size distribution functions on the magnetic entropy change ΔS for fine magnetic particle systems within the context of superparamagnetic theory. It provides the theoretical background of the magnetic and magnetocaloric properties of superparamagnetic systems. The model is taken of superparamagnetic fine particle with particle size distribution in magnetic media. Finally the method used in numerical calculations of the entropy change is presented on ideal superparamagnetic without interaction, then particles general superparamagnetic behavior of an aligned assembly of uniaxially anisotropic particles, then the effect of magnetic dipolar interaction is considered, finally the effect of both magnetic dipolar interaction an anisotropy constant is considered.

REFERENCES:

- [1] M.I. Kagnov and V.M. Tsukernik , <u>The nature</u> of magnetism, (Moscow), 1985.
- [2] R.M. Bozorth , <u>Ferromagnetism</u>, (D.Van Nostrand, Preceton, New Jersey), 1978.
- [3] A. Aharoni, <u>Introduction to the theory of</u> <u>ferromagnetism</u>, (Clarendon Press. Oxford), 1996.



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- [4] D.Craik, Magnetism Princibles and Applications, (John Wiley, New York), 1995.
- [5] P.R. Weiss, Phys. Rev. 74 (1948) 1493
- [6] J.S.Kouvel, Encyclopedia of Materials Science and Engineering, Ed. By M.B. Bever, (Pergamon Press, New York) (1986) 2703.
- [7] B.D.Cullity, Introduction to Magnetic Materials, (Addison-Wesley, New York), 1972.
- [8] S.Chikazumi, Physics of Ferromagnetism, (Clarendon Press, Oxford), 1997.
- [9] S.H. Charap, Magnetism and Metallurgy, Ed(s),
 A.E.Berkowitz and E. Kneller), Vol.2 (Academic Press, New York) (1969) 3.
- [10] J.S.Smart, Effective Field Theories of Magnetism, (W.B. Saunders Company, Philadelphia), 1966.
- [11] G.Busch, Lectures on Solid State Physics, (Pergamon Press, New York), 1976
- [12] C.B. Bean & J.D. Livingston, J. Appl. Phys, (1959), 120S.
- [13] R.Rosensweig;Ferrohydrodynamics, Cambridge University Press, New York), 1985.
- [14] R.D.Shull,R.D. McMicheal, L.J.Swartzendruber & L.H. Bennett, Magnetic_Properties of Fine

Particles, Edited by J. L. Dormann and D. Fiorani, (North Holland, 1992). P.161

- [15] D.Fiorani, Magnetic Properties Of Fine Particles, Edited by J. L Dormann and D. Fiorani, (North Holland, 1992). P.135.
- [16] M.Ozaki, Preparation and Properties of Well– Defined Magnetic Particles, (MRS Bulletin, United Kingdom, 1989) P.35.
- [17] I.S.Jacobs & C.P. Bean, in Magnetism, edited by G.T.Rado and R.D.Shull (Academic, New York, 1963), Vol.3, P.289.
- [18] R.P. Hudson, Princibles and Application of Magnetic Cooling, In Low Temperature Physics. Edited by C.J. Gorter, R.De Bruyn & D.De Klek, Vol2 (North-Holland, Amsterdam, 1972)
- [19] M.W. Zemansky, Temperatures Very Low and Very High, (Dover, New York), 1981.
- [20] P.V.E. Mcclintock, D.J. Meredith, and J.K.Wigmore, Matrer at Low Temperatures, (Blackie, Glasgw and London), 1984