Eur. Phys. J. B **10**, 237–245 (1999)

**THE EUROPEAN PHYSICAL JOURNAL B**

EDP Sciences


# Glass like magnetic alternating field susceptibility behavior of structurally frozen ferrofluids

D. Eberbeck[a]

Institut für Experimentelle Physik, Otto von Guericke Universität, Universitätsplatz 1, 39106 Magdeburg, Germany

Received 15 July 1998

**Abstract.** Four ferrofluids, distinct in size distribution and aggregate structure, were investigated. The relaxation time $\tau_{\rm m}(T)$, related to the temperature of susceptibility maximum, was fitted to a Vogel-Fulcher law. A mean ordering temperature, $T_0$, was calculated using magnetic particle parameters derived from the structure. It is assumed that at $T_0$ the particle moments of particle clusters correlate, leading to a spin glass-like transition. Hence, then dynamic slows down considerably, as indicated by a strong broadening of relaxation-time distribution. $T_0$ roughly agrees with the energy of competing interaction between particle moments, as calculated from the structure of particle aggregates. Differences between particle arrangements clearly influence the dispersion and absorption, particularly within the cluster phase.

**PACS.** 75.30.-m Intrinsic properties of magnetically ordered materials – 75.50.-y Studies of specific magnetic materials – 61.46.+w Clusters, nanoparticles, and nanocrystalline materials

## 1 Introduction

Ferrofluids are ensembles of disordered magnetic dipole moments. Owing to the anisotropy, the interactions between moments compete. Like in spin glasses, this may cause magnetic glass-like behavior at sufficient low temperatures [1–4]. The difficulties in understanding the spin glass phase [5,6] makes the studies of ferrofluids as model substances for glassy systems interesting [4]. Other non-magnetic disordered systems with competing interaction can also be simulated with them.

An advantageous circumstance is the possibility of many structure manipulations in ferrofluids[1]. This does not modify the type of interactions, a feature not met in spin glasses. Preventing particle aggregation, for example by dilution, one might estimate the moment and magnetic anisotropy of individual particles experimentally. X-ray scattering experiments give reliable information about particle-size distribution and particle formation within aggregates [8,9]. This gives a basis for the calculation of the macroscopic magnetic behavior.

To model spin glasses, it might seem disadvantageous that moments can experience individual blocking which leads to a different glass phenomenology. Further, the size of moments has a wide distribution in contrast to spin glasses. On the other hand, the study of ferrofluids allows to model systems which have precisely these ingredients. The comparison of magnetic structure and macroscopic properties of ferrofluids and spin glasses [4] provides a better understanding of the magnetic behavior of frozen ferrofluids.

Magnetization measurements [4] show that the superparamagnetic phase of ferrofluids crosses over gradually to a state with weak irreversibility. This phase seems governed by slow magnetic clusters. The existence of a phase with strong irreversibility at lower temperatures is suggested from the onset of hysteresis. The phenomenology of this second phase resembles more a spin glass phase than the former. Critical slowing down and aging measured on ferrofluids [2,3] support the existence of a true spin glass phase.

The development of the moment dynamics while the system crosses over from the superparamagnetic into the low temperature phase is investigated in the present paper. To interpret the results, information about the particle structure is used. The clear influence of aggregate structure on magnetic behavior is established by magnetization measurement [4]. The effect on the susceptibility at shorter time scales is investigated as well.

## 2 Method

A clear sign for the glassy state is a wide distribution $g(\tau)$ of relaxation times $\tau$. The dependence of the dynamic susceptibility on frequency is the expressed by generalized

[a] e-mail: dietmar.eberbeck@uni-magdeburg.medizin.de

[1] It can be partly realized easily. Structure changes like for example particle chaining in strong external fields can be achieved *in situ* [7,8].

Debye formulas [6]

$$\chi'(\omega) = \chi_S + \int_{\tau_{min}}^{\tau_{max}} \frac{\chi_T(\tau) - \chi_S(\tau)}{1+(\omega\tau)^2} g(\tau) \mathrm{dln}\tau,$$

$$\chi''(\omega) = \int_{\tau_{min}}^{\tau_{max}} \frac{\omega\tau\,(\chi_T(\tau) - \chi_S(\tau))}{1+(\omega\tau)^2} g(\tau) \mathrm{dln}\tau. \quad (1)$$

$\chi_T$ and $\chi_S$ are the static and adiabatic susceptibility, and $\omega = 2\pi f$, where $f$ is the frequency. For frequency values, $\omega = 2\pi/\tau$, in the middle of a broad and flat distribution, $g(\tau)$, on finds approximately [10]

$$\chi''(\omega) \approx -\frac{\pi}{2} \frac{\mathrm{d}\chi'}{\mathrm{dln}\omega}, \quad (2)$$

$$\approx -\frac{\pi}{2} (\chi_T(\tau) - \chi_S(\tau)) g(\tau). \quad (3)$$

The right hand side (3) is a measure of the spectral weight of the relaxation time $\tau$. The relation (2) is experimentally verified for spin glass systems near and above the transition temperature, $T_f$ [11,12].

The measurements of susceptibility were performed on a conventional alternating field susceptometer ACS7221 from Lake Shore. Estimates of the complex susceptibility, $\chi = \chi' + \mathrm{i}\,\chi''$, are based on an analysis of the induction voltage, $U \propto \mu_0 H_0\, \chi\, \mathrm{i}\omega\, \exp\{-\mathrm{i}\omega t\}$, of the measurement transformer. The output voltage is separated into in-phase and out-of-phase components with a lock-in amplifier.

## 3 Samples

### 3.1 Composition

The investigated ferrofluids are based on magnetite ($Fe_3O_4$) particles coated with a with a surfactant layer (oleic acid) and suspended in different solvents (Tab. 1). The samples were filled in glass cuvettes with a nearly cylindrical chamber. The ferrofluids were investigated in their frozen state only, *i.e.* after solidification of the solvents[2].

### 3.2 Particle and aggregate structure

The parameters of logarithmic normal size distribution (21) of the radii, $R$ (diameters $d$), of the core particles were determined using Small Angle X-ray Scattering (SAXS) experiments, assuming spherical particle shape [9] (Tab. 1). It was also possible to gain some information about the structure of particle aggregates which are built up due to high concentration and become developed during solidification of the solvent: The distances between particles within the aggregates diminish towards the minimal values $r = d + 2\delta$ ($d$-particle diameter), whereby the effective thickness of the tenside layer is $\delta \approx 2\,\mathrm{nm}$. Compact particle clusters which are more or less isolated from each other are present in the APG sample. The P17 aggregates have a porous, net-like structure. This aggregate structure is nearly homogeneous in median length scales, *i.e.* the aggregates are very extended. It was suggested that the width of the size distribution is a reason for the different kinds of aggregates [9].

For calculations of magnetic properties from the structure, it is necessary to know the magnitude of magnetic moments of particles, $m = M_S V$, which depends on particle volume, $V$, and its saturation magnetization, $M_S$. $M_S$ was derived from high field magnetization measurements (Tab. 1) and depends on the particle size (see also [13]).

Another indispensable parameter is the energy of magnetic anisotropy of the particle moments, $E_a = KV$. The anisotropy constant $K$ comprise the shape anisotropy, $K_s$ and the crystal anisotropy, $K_c \approx 15\,\mathrm{kJm^{-3}}$ [14] at $T \leq T_V \approx 100\,\mathrm{K}$ [3] [15]. The shape of the $Fe_3O_4$ particles is near spherical [16]. Deviations from perfectly spherical shape [7] lead to a shape anisotropy constant, $K_s \approx K_c$ [17]. Assuming that no correlation between crystal and shape anisotropy exists, the effective anisotropy was estimated to be $K = 20\,\mathrm{kJm^{-3}}$ with $\Delta K = 9\,\mathrm{kJm^{-3}}$.

### 3.3 Calculation of the susceptibility and the strength of competing interaction between dipoles

The susceptibility of an ensemble of non-interacting superparamagnetic dipole moments with ideal moment blocking was calculated [4] to

$$\chi(H,T,f) = \frac{M_S}{H} \frac{\int_0^{R_B(H,T,f)} f(R) R^3 L(H,T,R) \mathrm{d}R}{\int_R f(R) R^3 \mathrm{d}R} \cdot \quad (4)$$

$L$ is the Langevin function and $f$ is the logarithmic normal distribution of core radii. In equation (4) the thermal exception values of non-blocked moments are totalled. The contribution of the blocked moments, $\chi_{bl} = \frac{2}{3} M_S^2/2K \approx 3$ ($\beta = 1, T = 0$, maximum value) [18], is small (Fig. 1). At a given temperature the moments of particles with radii greater than $R_B(H,T,f) = \left[\frac{3\,kT}{4\pi K}\left(1 - \frac{H}{H_K}\right)^{-2} \ln(f\tau_0)\right]^{\frac{1}{3}}$ are blocked within observation time, $f^{-1}$, because of the Néel relaxation time

$$\tau = \tau_0\, \exp\left\{\frac{KV}{kT}\left(1 - \frac{H}{H_K}\right)\right\} \quad (5)$$

being greater than $f^{-1}$. $H_K = \frac{K}{\mu_0 M_S}$ is the anisotropy field and $\tau_0 = 10^{-10} \ldots 10^{-13}\,\mathrm{s}$ [19,20]. Simplifying, an uniaxial anisotropy, for which (5) is valid, was assumed.

Within the spin glass theory the freezing temperature, $T_f$, correlates with the energy of competing interaction.

[2] There are no sharp freezing temperatures of the oleic substances, kerosene and synthetic ester solvents (Tab. 1).

[3] $T_V$ is the size-dependent Vervey-temperature.

**Table 1.** Composition and structure as well as magnetic parameters of investigated ferrofluids.

| sample | solvent | volume-concentration | lognormal size distribution | | | | saturation magnetization of particles |
|---|---|---|---|---|---|---|---|
| | | $\beta$ [%] | $\langle d\rangle$ [nm] | $\Delta d$ [nm] | $\langle d^3\rangle^{1/3}$ [nm] | $\Delta d/\langle d\rangle$ | $M_S$ [kAm$^{-1}$] |
| P17 | kerosene | 12 | $5.1 \pm 0.3$ | $1.0 \pm 0.15$ | $5.3 \pm 0.3$ | $0.20 \pm 0.02$ | 320 |
| APG276 | synthetic ester | 2.7 | $5.3 \pm 0.3$ | $2.8 \pm 0.05$ | $6.8 \pm 0.2$ | $0.53 \pm 0.02$ | 390 |
| APG | synthetic ester | 8.7 | $5.3 \pm 0.3$ | $2.8 \pm 0.05$ | $6.8 \pm 0.2$ | $0.53 \pm 0.02$ | 390 |
| FDK | decan | 12 | $6.7 \pm 0.6$ | $3.4 \pm 0.15$ | $8.5 \pm 0.4$ | $0.51 \pm 0.02$ | 400 |

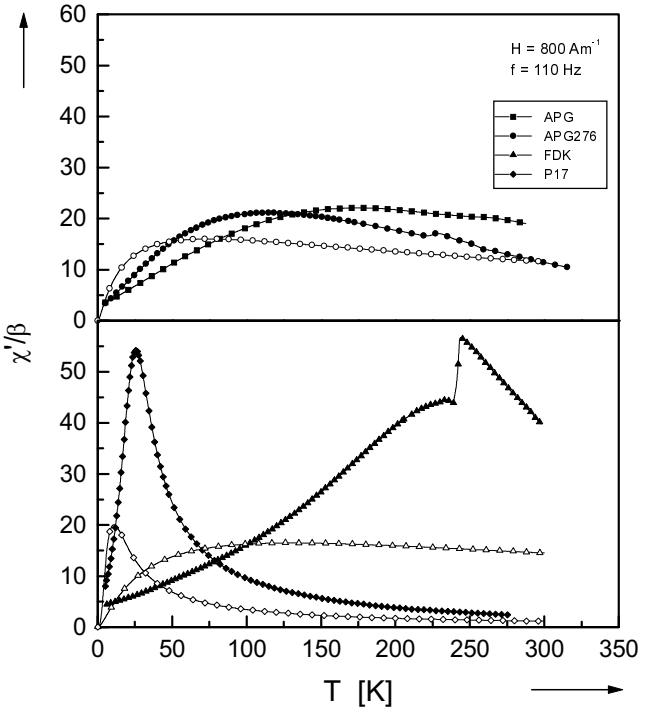


**Fig. 1.** Real part of the ac-susceptibility of the investigated ferrofluids (filled symbols). The open symbols are the corresponding values calculated for non-interacting superparamagnetic particles.

It is expressed by the dispersion of interaction potentials among the moments, $\Delta J$ [5]. For dipole systems with completely random moment orientation this energy dispersion was derived [4] to

$$\langle E_{\rm dd}^2\rangle^{1/2} = \frac{\sqrt{2}}{\sqrt{3}}\frac{\mu_0}{4\pi}\sqrt{\sum_{i=1}^{z}\frac{m_i^2 m_j^2}{r_{ij}^6}} \qquad (6)$$

(see appendix), *i.e.* $\langle E_{\rm dd}^2\rangle^{1/2} \mathrel{\widehat{=}} \Delta J$. Necessary information about the number $z$ of nearest neighbors and the distances $r$ between them were obtained from Small Angle X-ray Scattering experiments [9]. The Ising-like character of the moments is deduced from the ratio of interaction (6) to anisotropy energy, $E_{\rm a} = K\frac{\pi}{6}\langle d\rangle^3$ (Tab. 2). It is developed

**Table 2.** Calculated values of anisotropy energy and root mean square of the variance of dipole interaction between particle moments (6). The numbers of nearest neighbors, $z$, were roughly estimated from the assumed cluster structure.

| ferrofluid | $\langle d^3\rangle^{1/3}$ [nm] | $\langle E_{\rm dd}^2\rangle^{1/2}$ [K] | $E_{\rm a}$ [K] | $\frac{\langle E_{\rm dd}^2\rangle^{1/2}}{E_{\rm a}}$ |
|---|---|---|---|---|
| P17 | 5.3 | $12 \pm 2$ [a] | 113 | 0.11 |
| APG | 6.8 | $74 \pm 10$ [b] | 237 | 0.31 |
| APG276 | 6.8 | $45 \pm 7$ [c] | 237 | 0.19 |
| FDK | 8.5 | $174 \pm 20$ [d] | 460 | 0.38 |

[a] net-like aggregate structure, $z = 6 \pm 2$
[b] compact cluster structure, $z = 8 \pm 2$
[c] In APG276 no aggregation was observed during freezing, $z = 3 \pm 1$
[d] compact cluster structure, $z = 8 \pm 2$

mostly for the P17 with the smallest mean particle size ($\langle E_{\rm dd}^2\rangle^{1/2}/E_{\rm a} \approx \frac{1}{10}$). Interaction forces divert the moments only slightly from their easy axis direction. Due to the fast Néel relaxation (5) the moments can choose the one or the other orientation along the easy direction.

Now, it can be concluded that some spin glass-like ordering of ferrofluid moments occurs at the temperature, $T_0 \approx \langle E_{\rm dd}^2\rangle^{1/2}$, because an equivalent relation, $T_{\rm f} = \Delta J$, was established theoretically for Ising spin glasses and experimentally confirmed [5]. A lower ordering temperature is expected for Heisenberg spin glasses as for example given in [21]: $T_{\rm f} \approx 0.3\Delta J$.

## 4 Results and discussion

### 4.1 Temperature and field dependence

The ac-susceptibility exhibits a broad maximum at $T_{\rm m}$ (Fig. 1) like the low field quasistatic magnetization [4]. The shape of the $\chi'$ maximum, being similar to that of $\chi''$, is broader the wider the size distribution of small particles (Fig. 2). However, the obvious shape differences between APG and FDK, both having nearly the same dispersion

**Table 3.** Values of activation energy, $E_{\rm act}$, and temperature of susceptibility maximum $T_{\rm m}$ gained from experiments and from calculations for non-interacting moments. The calculated dipole interaction energy is taken from Table 2. The temperatures $T_0$ and $T_{\rm d}$ indicate the onset of moment ordering and strong extension of its relaxation times.

| ferrofluid | $\beta$ | $E_{\rm act}$ [K] | $E_{\rm act}^{\rm mod}$ [K] | $T_{\rm m}(0.1\,{\rm Hz})$ [K] | $T_{\rm m}^{\rm mod}(0.1\,{\rm Hz})$ [K] | $\langle E_{\rm dd}^2\rangle^{1/2}$ [K] | $T_0$ [K] | $T_{\rm d}$ [K] |
|---|---|---|---|---|---|---|---|---|
| P17 | 0.12 | 677 | 224 | $23 \pm 1$ | $8 \pm 4$ | $12 \pm 2$ | $15 \pm 5$ | $20 \pm 5$ |
| APG | 0.087 | 9210 | 1547 | $155 \pm 4$ | $56 \pm 25$ | $74 \pm 10$ | $100 \pm 29$ | $100 \pm 30$ |
| APG276 | 0.027 | 3386 | 1547 | $94 \pm 3$ | $56 \pm 25$ | $45 \pm 7$ | $38 \pm 28$ | $40 \pm 10$ |
| FDK | 0.12 | 12118 | 2700 | $212 \pm 10$ | $98 \pm 44$ | $174 \pm 20$ | $114 \pm 54$ | $170 \pm 30$ |

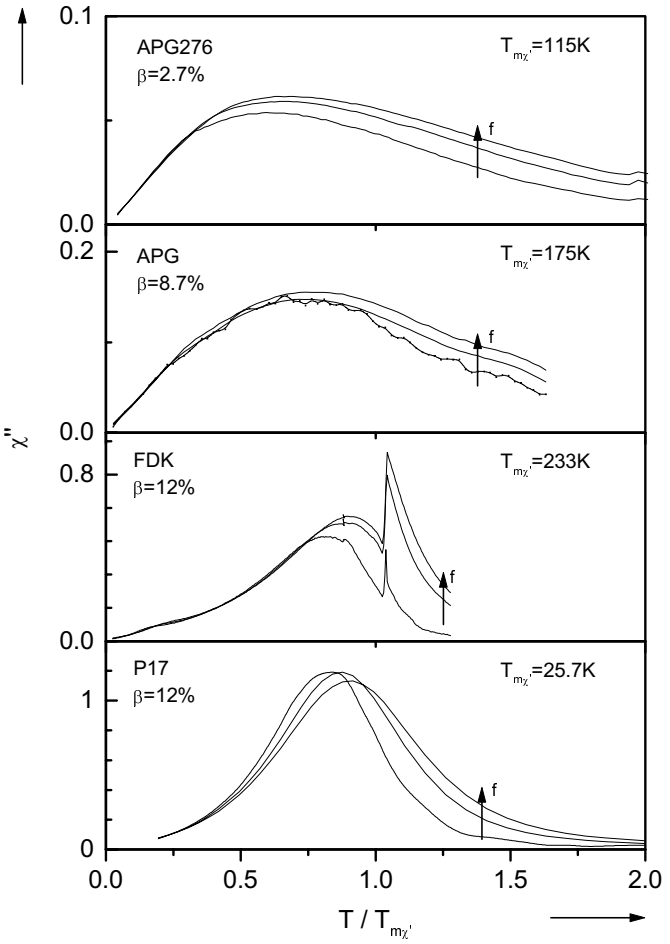


**Fig. 2.** Imaginary part of the ac-susceptibility at the frequencies $f = 10, 110, 400\,{\rm Hz}$. The temperature is rescaled with respect to the maximum temperature of $\chi'(110\,{\rm Hz})$.

of the particle size, show that other parameters, such as the structure of particle clusters, have a remarkable influence. Note that the shape of calculated $\chi(T)$-curves of APG and FDK are very similar (Fig. 1).

A calculation of the real part of susceptibility (4) for given samples was possible because the particle size distribution, saturation magnetization (Tab. 1) and magnetic anisotropy constant of particles (Sect. 3.2) were known. Here, the dipole interaction between particle moments were not taken into account. From comparison with calculated data (Fig. 1), it is concluded that the dipole-dipole interaction is indispensable to explain the values of the temperatures of the susceptibility maxima, $T_{\rm m}$, which are higher than the corresponding $T_{\rm m}^{\rm mod}$ (Tab. 3).

The susceptibility maximum in canonical spin glasses at $T_{\rm m}$ is sharp. It is assumed that a phase transition occurs at $T_{\rm f} \approx T_{\rm m}$ in the limit $H \to 0$, indicated by the divergence of the non-linear susceptibility [6,22]. For the purpose of explaining the very broad maximum for frozen ferrofluids, the following working hypothesis will be given:
Moments belonging to various particle clusters undergo a quasistatic freezing transition at individual different temperatures. The correlation radius of the particle moments around $T_{\rm m}$ remains finite, *i.e.* roughly limited to the boundaries of particle clusters.

From the field dependence of ac-susceptibility it is confirmed that the origin of susceptibility maximum of ferrofluids is distinguished from that of canonical spin glasses. The susceptibility of spin glasses at $T_{\rm m}$ diminishes remarkably when a small dc-field is superimposed [23]. For ferrofluids a decrease $\chi$ sets in for fields $H > 800\,{\rm Am}^{-1}$, only (Fig. 3). The non-sensitivity of ac-susceptibility to small fields is plausible because no sign of its divergence at $T_{\rm m}$ exists. Here connections to the $T_{\rm m}(H)$-dependence may exist. At low fields ($80 < H < 2000 \ldots 3000\,{\rm Am}^{-1}$) the temperature of susceptibility maximum, $T_{\rm m} \approx 145\,{\rm K}$, is nearly independent of the field[4] [4].

### 4.2 Frequency dependence

The non-zero values of $\chi''$ indicate the non-equilibrium magnetic behavior in a wide temperature range (Fig. 2). In this range there is also an irreversibility of low field static magnetization [4].

Considering the frequency dependence of $T_{\rm m}$, the magnetic state around the susceptibility maximum at $T_{\rm m}$ will be enlightened. $T_{\rm m}^{-1}(f)$ shows a linear dependence on $\lg f$ (Figs. 4, 5). This is typical of systems consisting of independent relaxing entities. Hence, the relaxation time may

[4] By calculation (4) it was shown that this behavior is also typical of an ensemble of non-interacting moments, if their individual relaxation times (5) exhibit some distribution.

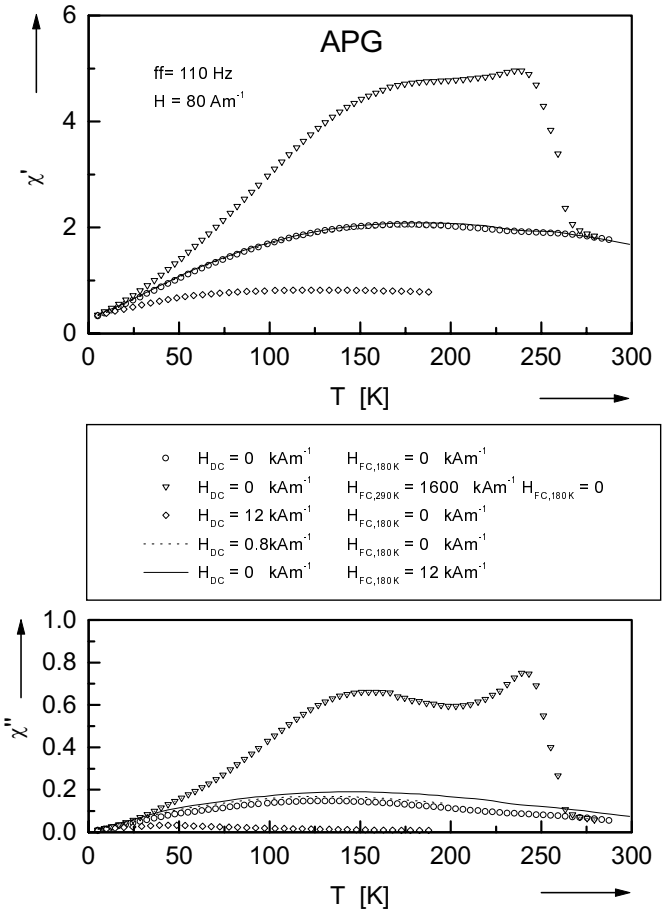


**Fig. 3.** Temperature dependence of the complex ac-susceptibility of APG. The superimposed dc-fields and cooling conditions are different.

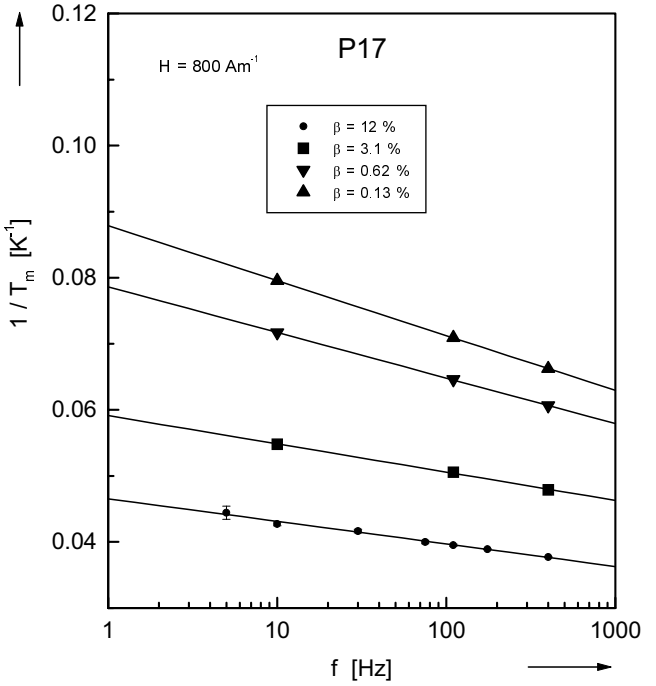


**Fig. 4.** Frequency dependence of the inverse temperature of the susceptibility maximum for P17 ferrofluid samples having different magnetite concentrations.

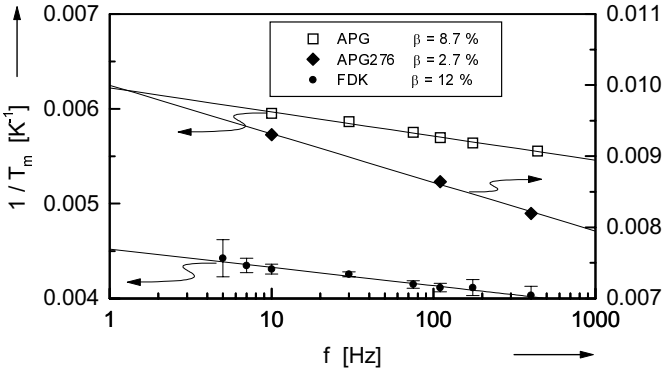


**Fig. 5.** Frequency dependence of the inverse temperature of the susceptibility maximum for FDK and APG ferrofluids. $T_\mathrm{m}$ of FDK is estimated from $\frac{\mathrm{d}\chi}{\mathrm{d}T}$ because $T_{\mathrm{m},\chi}$ is greater than the melting temperature of decan (240 K) at high frequencies. Here, the relation, $T_{\mathrm{m},\chi} - T_{\mathrm{m},\frac{\mathrm{d}\chi}{\mathrm{d}T}} \approx 70\,\mathrm{K}$, found for low frequencies, was used.

be described by the Arrhenius law,

$$\tau = \tau_0 \exp\left\{\frac{E_\mathrm{act}}{kT}\right\}, \tag{7}$$

with the microscopic relaxation time, $\tau_0 = 10^{-10} \ldots 10^{-13}\,\mathrm{s}$, [5] and the height of the energy barrier, $E_\mathrm{act}$, being independent of temperature. Equation (7) corresponds to (5) for small fields with the anisotropy energy of the magnetite particles $E_\mathrm{act} = KV$.

For spin glass like systems, a wide distribution of relaxation times, $g(\tau)$, is characteristical. The average relaxation time is defined by $\bar{\tau} = f_\mathrm{max}^{-1}$ with $f_\mathrm{max}$ being the frequency at which $\chi''(f)$ is at its maximum. At the temperature $T_\mathrm{m}(f)$ where $\chi_\mathrm{f}'(T)$ is at its maximum for a given measurement frequency, $f$, it will be defined

$$\tau_\mathrm{m} = f^{-1}. \tag{8}$$

With (8) the equation (7) becomes

$$T_\mathrm{m}^{-1}(f) = -\left(\frac{E_\mathrm{act}}{k}\right)^{-1} \ln(\tau_0 f). \tag{9}$$

$E_\mathrm{act}$ is some weighted mean with

$$\tau_\mathrm{m} > \bar{\tau} \tag{10}$$

because the maximum of $\chi_\mathrm{f}''(T)$ appears at a lower temperature than that of $\chi_\mathrm{f}'(T)$ (Fig. 2) and because the relaxation time is usually smaller at higher temperature. Consequently, the values, $E_\mathrm{act}^\mathrm{mod}$, calculated according (9) for non-interacting superparamagnetic particles (Tab. 3) are greater than the mean anisotropy energy of particles, $E_\mathrm{a}$ (Tab. 2).

The third characteristic relaxation time of $g(\tau)$ is the maximum value, $\tau_{\max}$. If $\tau_{\max}(T)$ reaches the measurement time, $f^{-1}$, then $\chi'_{\rm f}(T)$ begins to divert from the thermodynamic equilibrium value, $\chi_{\rm T}$, and absorption sets in ($\chi'' > 0$).

The values, $\tau_{\max}(T)$, can be fitted to a Vogel-Fulcher law,

$$\tau = \tau_0 \exp\left\{\frac{E_{\rm act}}{k(T - T_0)}\right\}, \tag{11}$$

for spin glasses [6,24] and also for ferrofluids [3] with reasonable parameters for $E_{\rm act}$ and $\tau_0$. The divergence of $\tau_{\max}(T)$ indicates a critical slowing down at $T_0$ which hints at a static phase transition into the glass phase. For spin glasses the development of $\tau_{\rm m}(T)$ is qualitatively similar to that of $\tau_{\max}(T)$ [6], *i.e.* $T_{\rm m}^{-1}(f)$ has a non-zero static ($f \to 0$) limit [23].

$\tau_{\max}$ is not measurable for all ferrofluids because $\chi'' > 0$ at all temperatures below the freezing points, except for P17. Therefore $\tau_{\rm m}(T)$ will be investigated. The difference $T(\tau_{\max} = f^{-1}) - T(\tau_{\rm m} = f^{-1})$ is larger for ferrofluids (P17: $T(\tau_{\max}) \approx 76\,{\rm K}; T(\tau_{\rm m}) \approx 26\,{\rm K}$) than for spin glasses. Following the working hypothesis, this is likely to be connected with the wide distribution of quasistatic freezing temperatures of moments within the various clusters. In order to investigate the behavior of magnetic particle moments at $T_{\rm m}$, $\tau_{\rm m}$ should be considered. In addition, this reflects the contribution of the *representative* clusters on the slowing down of the dynamic because at $T_{\rm m}$ a relatively strong deviation of the susceptibility from $\chi_{\rm T}$ sets in. This is confirmed by the difference between the field cooled and the zero field cooled magnetization [4].

Indeed, the activation energy $E_{\rm act}$, calculated by the fitting of $\tau_{\rm m}(T)$ to the Arrhenius law (9) (Figs. 4, 5), is much greater than $E_{\rm act}^{\rm mod}$, derived from model (4) by an analogous treatment of $T_{\rm m}^{\rm mod}(f)$ (Tab. 3). Because the dynamic behavior of the particle moments is the matter of interest, *i.e.* the existence of some mean ordering temperature, $T_0$, $\tau_{\rm m}(T)$ must be fitted to (11) [5]. The activation energy should be represented by $E_{\rm act}^{\rm mod}$ ensuring that $T_0 \to 0$ in the limit of vanishing interaction. With (8) and with $E_{\rm act}^{\rm mod} = -kT_{\rm m}^{\rm mod}\ln(\tau_0 f)$ the formula,

$$T_0 = T_{\rm m}(f) - T_{\rm m}^{\rm mod}(f), \tag{12}$$

results from (11). $\tau_0 = 10^{-11}\,{\rm s}$ was applied in good agreement with the measured values for fine particles [3,18]. If $T_0 > 0$ exists, the linear dependence of $T_{\rm m}^{-1}$ on $\lg f$ (Figs. 4, 5) may be an artifact of the small measured frequency range.

The ordering temperature in (11), $T_0$, is a measure of the interaction energy between the moments. The values of $T_0$ are in rough agreement with $\langle E_{\rm dd}^2\rangle^{1/2}$ (Tab. 3). The confirmation of the prediction, $T_0 \approx \langle E_{\rm dd}^2\rangle^{1/2}$ (Sect. 3.3) supports the hypothesis that the moments cross over into a spin glass-like phase. Because $\langle E_{\rm dd}^2\rangle^{1/2}$ was calculated for closely packed particles with random moments (see appendix), one may conclude that this glass phase is restricted to particle clusters, comprising nearly randomly oriented moments. Because the moments of ferrofluids are not perfectly Ising-like, deviations from the relation, $T_0 = \langle E_{\rm dd}^2\rangle^{1/2}$, may occur. FDK for which $\frac{\langle E_{\rm dd}^2\rangle^{1/2}}{K\langle V\rangle} \approx 0.4$ (Tab. 2) exhibits a comparatively weak Ising property. This may be the reason for the most negative value of the difference, $T_0 - \langle E_{\rm dd}^2\rangle^{1/2}$.

Because the moment freezing around $T_{\rm m}$ is restricted to particle clusters with a finite number of moments, a divergence of the relaxation time, $\tau_{\max}(T)$ or $\tau_{\rm m}(T)$, to infinity can not be expected. This means that the smeared phase transition near $T_0$ is quasistatic (Sect. 4.1). It is presumed that the distribution of relaxation time reaches large values, determined by the size of the clusters.

While temperature increases, the relaxation becomes faster as follows from absorption values, $\chi''(f)$, being greater at higher frequencies (Fig. 2). At temperatures lower than some limit, $T_{\rm d}$ (Tab. 3), $\chi''$ becomes nearly independent of $f$ (Fig. 2). From equation (3) follows that all relaxation processes have the same spectral weight within the experimental time window, $f_{\max}^{-1} \ldots f_{\min}^{-1}$. This is verified by the dominant real part susceptibility, $\chi'(f) \propto \ln f$ [6]. It is noteworthy that for P17 with smallest particle size distribution and the more extended aggregates the absorption at low frequencies has a higher weight (Fig. 2). This tendency is also found for chain-like aggregates (Sect. 4.3.2).

The relation, $T_{\rm d} \approx T_0$, indicates that the extension of the relaxation time distribution is related to a spin glass-like moment ordering at $T_0$ as suggested above. An analogous relation, $T_{\rm d} \approx T_{\rm f}$, for the spin glass $(Eu_{0.2}Sr_{0.8})S$ was found [24].

The relative small split effect, connected with the sensitivity of $\chi''$ to phase angle correction, makes precise determination of $T_{\rm d}$ difficult. The hump in $\chi''(T)$ for FDK at about 40 K (Fig. 2) is likely to be connected with some change in structure within magnetite, which occurs at 48 K for bulk material [26]. Soeffge and Schmidtbauer have measured a jump in magnetization for a magnetite single crystal at this temperature [27]. This may be also a reason for the imperfectly defined $T_{\rm d}$ in the case of APG.

When at temperatures, $T < T_0$, clusters of near randomly oriented moments exist, the following questions remain open: Which magnetic structure exists in the temperature range $T > T_0$? Can it cause energy barriers being of order of $T_{\rm m}$? For this low irreversibility phase the following hypothetical cluster picture is proposed:
Ferromagnetic-like short range order dominates at higher temperatures, concluded from positive Curie temperature, $\Theta$, being of the order of $T_{\rm m}$. The anisotropic dipole-dipole

[5] Shtrikman and Wohlfarth have shown the validity of (11) to get an ordering temperature for particle moments like these in the case of weak interaction, *i.e.* $T_0 \ll E_{\rm act}$ [25]. This condition is nearly fulfilled, shown by the ratio $\frac{\langle E_{\rm dd}^2\rangle^{1/2}}{E_{\rm a}}$ (Tab. 2).

[6] In contrast to $\chi''$, the dominating real part, $\chi'$, is insensitive to phase angle corrections being determined by measuring equipment. It allows the value of imaginary part, $\chi''$, to be controlled by means of equation (2) (Tab. 4).

interaction leads to ferro- or antiferromagnetic-like correlation between neighboring moments, depending on its mutual orientation. However, the ferromagnetic coupling between two moments causes a two times higher energy gain (18) than the antiferromagnetic one. Consequently, at first the ferromagnetic correlations by decreasing the temperature were realized. The moments which are not suitably arranged in favor of ferromagnetic couplings remain agitated, *i.e.* they have small thermodynamic expectation values. Magnetic clusters with a ferromagnetic-like or asperomagnetic order may arise. The interaction between asperomagnetically ordered moments may exceed $\langle E_{\mathrm{dd}}^2\rangle^{1/2}$, explaining the high $T_{\mathrm{m}}$ values. When the frustrated moments[7] begin to freeze at further reduced temperature, they disturb the asperomagnetic order. Hence, the interactions between all moments become strongly competitive and the system enters into a glass-like phase.

The considerable magnitude of the cluster moments may be the reason for the dc-field influence which is stronger in the cluster phase (around $T_{\mathrm{m}}$) than in the glassy state at low temperatures ($T \leq 40\,\mathrm{K}$) (Fig. 3). This is also concluded from the $T_{\mathrm{m}}(H)$-behavior: $1 - T_{\mathrm{m}}/T_{\mathrm{m0}} \propto H^{2/5}$ at $T_{\mathrm{m}}(H) \geq 60 \pm 15\,\mathrm{K}$ [4]. The interaction between the resulting cluster moments is small because of its low saturation magnetization.

How does the magnetic system behave at lower temperatures? It is suggested that the clusters of frozen moments percolate at $T < T_0$. That is why the interaction among the moments belonging to the inter-cluster space is reduced because of the higher particle distances. Indeed, a cross over to strong irreversibility was found by magnetization measurements at high fields [4]: Magnetic hysteresis sets in at temperatures between 40 and 70 K for APG. The measured $T_{\mathrm{m}}(H)$ function changes its course at the temperature, $T = 60 \pm 15\,\mathrm{K}$, which is lower than $T_0$.

## 4.3 Influence of topology

### 4.3.1 Variation of concentration

Different degrees of particle concentrations were realized by diluting the P17 ferrofluid with kerosene. Due to the enhanced particle distances the mean interaction energy diminishes and the temperature of susceptibility maximum $T_{\mathrm{m}}$ decreases (Fig. 4). The concentration dependent maximum temperature, $T_{\mathrm{m}}(\beta)$, was fitted by a power law with the result

$$T_{\mathrm{m}}(\beta) = (29 \pm 4)\,\beta^{(0.37\pm0.12)} + (10 \pm 2). \qquad (13)$$

The freezing temperature of spin glasses, $T_{\mathrm{f}}$, obeys $T_{\mathrm{f}}(\beta) \propto \beta$ for $\beta < 1\mathrm{at}\%$ and $T_{\mathrm{f}}(\beta) \propto \beta^{2/3}$ for $1 \leq \beta \leq 10\mathrm{at}\%$. The decrease in the power reflects the influence of the non-competing short range interaction [5]. The comparatively slow change of the maximum temperature of the ferrofluids, $\propto \beta^{0.37}$, is likely to be connected with the existence of small particle clusters within the very diluted samples [9]. The threshold value of 10 K in equation (13) should approach the maximum temperature, $T_{\mathrm{m}}^{\mathrm{mod}} = 8 \pm 4\,\mathrm{K}$ (Tab. 3), calculated for non-interacting particles. The difference may be caused by the presence of particle clusters as well as the uncertainty of the anisotropy constant, $K$, and of the exact functional form of $T_{\mathrm{m}}(\beta)$.

[7] Ferro- and antiferromagnetic bonds are nearly equally distributed.

**Table 4.** ac-susceptibility for investigated ferrofluids with various topological structures.

| ferrofluid sample | $\beta$ [%] | $T$ [K] | $\chi'$ | $\chi''$ | $\frac{\chi''}{\chi'}$ | $\tilde{\chi}''$ [a] | $\frac{\tilde{\chi}''}{\chi'}$ |
|---|---|---|---|---|---|---|---|
| $f = 10\,\mathrm{Hz}$ | | | | | | | |
| APG | 8.7 | 150 | 2.20 | 0.15 | 0.070 | 0.184 | 0.08 |
| FDK | 12 | 180 | 5.00 | 0.47 | 0.094 | 0.40 | 0.08 |
| P17 | 12 | 23 | 8.00 | 1.20 | 0.150 | 0.91 | 0.11 |
| P17 (FC[b]) | 12 | 23 | 21.0 | 5.00 | 0.238 | | |
| $f = 400\,\mathrm{Hz}$ | | | | | | | |
| P17 | 12 | 23 | 5.20 | 1.2 | 0.230 | | |
| P17 (FC) | 12 | 23 | 12.5 | 3.5 | 0.280 | | |
| $f = 110\,\mathrm{Hz}$ | | | | | | | |
| APG | 8.7 | 150 | 1.9 | 0.15 | 0.079 | | |
| APG (FC) | 8.7 | 150 | 4.3 | 0.67 | 0.156 | | |

[a] $\tilde{\chi}'' = -\frac{\pi}{2\cdot\ln 10}\frac{\mathrm{d}\chi'}{\mathrm{d}\lg f}$.

[b] The particle system was frozen in the field $H_{\mathrm{FC}} = 16\,\mathrm{kAm^{-1}}$.

### 4.3.2 Chain like particle aggregates

If the samples are being cooled in presence of a strong magnetic field, $H_{\mathrm{FC}} = 1600\,\mathrm{kAm^{-1}}$, to a temperature below solidification point of carrier liquid, the particles build chains remaining stable after removal of the freezing field [7,8]. The ferromagnetic order between moments belonging to the same chain increases. This is experimentally verified by the Curie temperature, $\Theta_{\mathrm{FC}} = 43\,\mathrm{K}$, which is significantly greater than for isotropic particle order ($\Theta_{\mathrm{ZFC}} = 27\,\mathrm{K}$). The particle-chain structure causes a $2\ldots3$-fold enhancement of susceptibility at temperatures around the susceptibility maximum (Fig. 3, Tab. 4). Decreasing the temperature, the correlation radius of magnetic moments increases due to the reduction of the thermal disorder. Then interaction between chains, caused by their high resulting magnetic moments, sets in. This interaction has a more competitive property than that between the chained particles. This may explain why the difference in the $T_{\mathrm{m}}$-values, $\Delta T_{\mathrm{m}} = T_{\mathrm{m,FC}} - T_{\mathrm{m,ZFC}}$, remains small (P17: $T_{\mathrm{m,FC}}(110\,\mathrm{Hz}) = 26.5\,\mathrm{K}$, $\Delta T_{\mathrm{m}} = 3.2\%$, APG: see Fig. 3).

For chain-like structures the relative absorption, $\chi''/\chi'$, is $1.5\ldots2$ times higher than in samples with isotropic particle arrangement (Tab. 4). Particle chaining

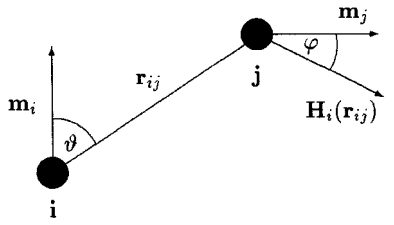


**Fig. 6.** Sketch of two interacting magnetic dipole moments.

in APG leads to a stronger enhancement of the relative absorption (Tab. 4) because $\chi''/\chi'$ is significantly smaller for APG than for P17 in the case of isotropic structure. This is probably connected with the smaller extension of the aggregates of APG [9]. From these results (Tab. 4) it also follows that the increase of absorption is more pronounced at low frequencies.

## 5 Conclusion

The results of this report and [4] give a picture of how the superparamagnetic moments of solidified ferrofluids could enter into a spin glass-like state. Non-equilibrium dynamic of moments is observed over a wide temperature range. This is achieved to a considerable part by interaction between moments and not only by superparamagnetic blocking. The slowing down of the dynamics is caused by the correlation of the moments and creates the maximum of susceptibility at $T_\mathrm{m}$. The correlation sets in first within existing particle clusters where the interaction is stronger than in the inter-cluster phase. The various sizes and structures of the aggregates cause some distribution of ordering temperatures. This is probably responsible for the broad shape of the susceptibility maximum.

From the agreement between the mean ordering temperature, $T_0$, and the calculated interaction energy, $\langle E_\mathrm{dd}^2\rangle^{1/2}$, it is concluded that glass like moment correlation occurs at $T_0$, namely within clusters. This may produce a finite jump of relaxation times. Only when thermal energy decreases below the interaction energy of the inter-cluster phase, a percolation of spin glass-like order through the entire sample is possible. This is supported by the onset of strong irreversibility at temperatures lower than $T_0$.

Homogenization of the structure and a more accurate knowledge of local anisotropy seems to be necessary for a successful quantitative study of phase transitions in disordered systems like these.

It was shown that particle aggregate structure has a significant influence on susceptibility, especially at higher temperatures, where the radius of magnetic correlations is small. Extended and chain like aggregates support ferromagnetic like short range coupling and the absorption of alternating magnetic fields, in particular for low frequencies.

## Appendix: Calculation of the interaction energy of magnetic dipoles

The dipole interaction potential of a dipole moment, $\mathbf{m}_j$,

$$E_\mathrm{dd} = -\mu_0 \mathbf{m}_j \cdot \mathbf{H}_i(\mathbf{r}_{ij}), \tag{14}$$

in a magnetic field,

$$\mathbf{H}_i(\mathbf{r}_{ij}) = \frac{1}{4\pi}\left(3\frac{(\mathbf{m}_i\cdot\mathbf{r}_{ij})\,\mathbf{r}_{ij}}{r_{ij}^5} - \frac{\mathbf{m}_i}{r_{ij}^3}\right), \tag{15}$$

produced by another moment, $\mathbf{m}_i$, is expressed in spherical coordinates (Fig. 6) by

$$E_\mathrm{dd}(\varphi,\vartheta) = -\mu_0 m_j H_i(\vartheta, r_{ij})\cos\varphi \tag{16}$$

with

$$H_i(\vartheta, r_{ij}) = \frac{1}{4\pi}\frac{m_i}{r_{ij}^3}\sqrt{3\cos^2\vartheta + 1}. \tag{17}$$

In a system with random moment correlations the mean value of (16) is zero, but not the mean value of

$$E_\mathrm{dd}^2(\varphi,\vartheta) = \left(\frac{\mu_0}{4\pi}\right)^2 \frac{m_i^2 m_j^2}{r_{ij}^6}\left(3\cos^2\vartheta + 1\right)\cos^2\varphi. \tag{18}$$

$\langle E_\mathrm{dd}^2\rangle$ is equivalent to the variance of exchange coupling for spin glasses, $(\Delta J)^2 = \langle (J - \langle J\rangle)^2\rangle$. The transition temperature for Ising spin glasses is roughly $T_\mathrm{f} = \Delta J$ [28]. In system with randomly frozen moments, $\mathbf{m}_j$, the average in (18) must be performed over $\vartheta$ *and* $\varphi$. If the short range order is homogeneous, *i.e.* all sites $j$, surrounding particle $i$, are occupied with the same probability, then $\langle 3\cos^2\vartheta + 1\rangle = 2$. Simultaneously, each moment can bear a random direction leading to $\langle\cos^2\varphi\rangle = 1/3$.

If the local field, $H$, is created by $z$ neighbors ($H = \sqrt{\sum_i^z H_i^2}$ if $\mathbf{H}_i$ are oriented at random), equation (18) becomes

$$\langle E_\mathrm{dd}^2\rangle^{1/2} = \frac{\sqrt{2}}{\sqrt{3}}\frac{\mu_0}{4\pi}\sqrt{\sum_{i=1}^{z}\frac{m_i^2 m_j^2}{r_{ij}^6}}. \tag{19}$$

This is the mean interaction potential of randomly frozen, non-movable moments.

Luttinger and Tisza have reported the possibility of a ferromagnetic order in dipole systems with a periodic cubic structure, such as a fcc or bc lattice [29]. But, the local random anisotropy prevents an order like this at any reasonable concentration [30].

Although the dipole-dipole interaction is long ranging ($\propto r^{-3}$), the effective interaction in random moments systems is restricted to the nearest neighbors. The contribution of the next nearest neighbors to the field (15) is negligible compared with that of nearest neighbors because $H$ is related to the variance of $H_i$. Note that $H_i$ enter in the sum of (19) proportional to $r^{-6}$.

With regard to the distribution of the magnitude of the moments, $f(R,\mu,\sigma)$, the interaction energy (19) may be calculated to

$$\langle E_{\rm dd}^2\rangle^{1/2} = \frac{\sqrt{2}}{\sqrt{3}}\frac{\mu_0}{4\pi}\sqrt{z} \times \sqrt{\int_{R_i}\int_{R_j} f(R_i,\mu,\sigma)f(R_j,\mu,\sigma)\frac{m_i^2 m_j^2}{r_{ij}^6}\,{\rm d}R_i{\rm d}R_j}, \quad (20)$$

$\mu$ and $\sigma$ are the parameters of the lognormal size distribution,

$$f(R,\mu,\sigma) = \frac{1}{\sqrt{2\pi}\sigma R}\exp\left\{-\frac{(\ln(R)-\mu)^2}{2\sigma^2}\right\}, \quad (21)$$

of particle radii, $R$.

## References


1. W. Luo, S.P. Nagel, T.F. Rosenbaum, R.E. Rosensweig, Phys. Rev. Lett. **67**, 2721–2724 (1991).
2. T. Jonsson, J. Mattsson, C. Djurberg, F.A. Khan, P. Nordblad, P. Svedlindh, Phys. Rev. Lett. **75**, 4138–4141 (1995).
3. C. Djurberg, P. Svedlindh, P. Nordblad, Phys. Rev. Lett. **79**, 5154–5156 (1997).
4. D. Eberbeck, H. Ahlers, J. Magn. Magn. Mater. (submitted).
5. J.A. Mydosh, *Spin Glasses-An Experimental Introduction* (Taylor and Francis, London-Washington, 1993).
6. K. Binder, A.P. Young, Rev. Mod. Phys. **58**, 801–976 (1986).
7. R. Anthore, C. Petipas, J. Phys. Colloq. France **38**, C2-203–209 (1977).
8. J. Bläsing, G. Strassburger, D. Eberbeck, Phys. Stat. Sol. A **146**, 595–602 (1994).
9. D. Eberbeck, J. Bläsing, J. Appl. Cryst. (submitted).
10. L. Lundgren, P. Svedlindh, O. Beckman, J. Magn. Magn. Mater. **25**, 33 (1981).
11. L. Lundgren, P. Svedlindh, O. Beckman, J. Magn. Magn. Mater. **31-34**, 1349–1350 (1983).
12. P. Svedlindh, P. Granberg, P. Nordblad, L. Lundgren, H.S. Chen, Phys. Rev. B **35**, 268–272 (1987).
13. J.M.D. Coey. J. Appl. Phys. **49**, 1646–1652 (1978).
14. *Landolt-Börnstein*, edited by K.-H. Hellwege (Springer Verlag, Berlin, Heidelberg, New York, 1970), Vol. 4 of *3*, pp. 67–74.
15. S. Mørup, H. Topsoe, J. Magn. Magn. Matter. **31-34**, 953 (1983).
16. S. Itoh, Y. Endoh, S. Taketomi, S. Chikazumi, J. Magn. Magn. Matter. **103**, 126–128 (1992).
17. U. Hartmann, H.H. Mende, J. Magn. Magn. Mater. **45**, 409–414 (1984).
18. J.L. Dormann, D. Fiorani, E. Tronc, Magnetic relaxation in fine-particle systems, Number XCVIII in Advances in Chemical Physics (John Wiley & Sons, 1997), pp. 283–494.
19. R.W. Chantrell, K. O'Grady, A. Bradbury, S.W. Charles, J. Popplewell, J. Phys. D: Appl. Phys. **18**, 2505–2517 (1985).
20. S. Mørup, E. Tronc, Phys. Rev. Lett. **72**, 3278–3281 (1994).
21. K. Binder, *in Ordering in strongly fluctuating Condensed Matter Systems*, edited by T. Riste (Plenum Publishing Corporation, 1980), pp. 423–444.
22. P. Nordblad, P. Svedlindh, in *Spin Glasses and Random Fields*, edited by A.P. Young, Series on Directions in Condensed Matter Physics, Vol. 12 (World Scientific, Singapore, New Jersey, London, Hong-Kong, 1998), pp. 1–27.
23. H. Maletta, J. Magn. Magn. Mater. **24**, 179–185 (1981).
24. D. Hüser, L.E. Wenger, A.J. van Duyneveldt, J.A. Mydosh, Phys. Rev. B **27**, 3100–3103 (1983).
25. R.W. Chantrell, E.P. Wohlfarth, J. Magn. Magn. Mater. **40**, 1–11 (1983).
26. K.P. Belov, UFN **163**, 53–65 (1993).
27. F. Söffge, E. Schmidtbauer, J. Magn. Magn. Mater. **24**, 54–66 (1981).
28. S. Mørup, Europhys. Lett. **28**, 671–676 (1994).
29. J.M. Luttinger, L. Tisza, Phys. Rev. **70**, 11 (1946).
30. H. Zhang, M. Widom, Phys. Rev. B **51**, 8951–8957 (1995).