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EFFECT OF ANOMALOUS PARTICLES DIFFUSION DAMPING IN FERROFLUID NEAR CURIE TEMPERATURE

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Abstract. The structure and anomalous dynamics of the ferrofluid have been studied around the 2nd order transition temperature of the magnetic phase (T_C~20°C) by neutron spin-echo in nanosecond time-range to recognize the interaction of the nuclear and magnetic subsystems. The strong damping of the particles mobility due to critical magnetic fluctuations is discussed.

Key words: ferrofluid, low T_c, dynamics, spin-echo.

INTRODUCTION

In order to understand the ferrofluids (FF) behavior, distinguishing them from nonmagnetic colloids, we have to study the FF lost dipolar forces. Really most FF possess magnetic phase Curie temperature (Fe_3O_4, T_C=585°C) far above the region of the stable colloidal state. The critical or paramagnetic state cannot be realized due to colloid destruction. Any theory of FF-particles assembly *via* dipole interactions, should be based only on microscopic data [1-4] for FF in the colloidal state in both regions ($T<T_C$, $T\geq T_C$). In order to understand more in detail the role of the dipolar forces a sample with low T_C ($T_C\approx 20$°C) was prepared and investigated by the NSE technique.

EXPERIMENTAL

Ferrite $Mn_{0.3}Zn_{0.7}Fe_2O_4$ ($T_C\approx 20$°C) particles were synthesized [5] and FF prepared from single-domain particles (8% vol., stabilized by oleic acid in dodecane). First we found the particles size R_P=10 nm ($\Delta R_P/R_P$ = 0.5) from dynamic light scattering. Neutron scattering from FF, nondisturbed by the magnetic field, at temperatures T = 7÷150°C (PNPI: SANS-"Membrane"; RISSPO: "Yellow submarine") carries mainly the information on the nuclear subsystem (intensity I_n), because of the weak contribution $I_m \sim 10^{-4} I_n$ of the magnetic scattering to the total intensity $I_t = I_n + I_m \approx I$ at low ferrite magnetization (M = 16Gauss, 17°C). The scattering reflects mostly the influence of the weak (but long-range) magnetic forces on the nuclear subsystem.

The temperature dependence of the sample transmission (neutron wavelength $\lambda = 0.3$nm) on heating demonstrates the intensity decrease and drop $\Delta I_n/I_n \sim -5\%$ at $T \sim T_C$ (Fig.1), because of the neutrons leaving the central detector aperture ($\Delta\Omega \sim 10^{-5}$st.rad.) when some large colloidal structures (with size $\geq 10^2$nm) are broken at $T \geq T_C \approx 20°C$. Due to a small magnetic contribution $I_m \sim 10^{-2}(\Delta I_n/I_n)$ the drop of the scattering intensities in the region q = 0.04-0.8nm^{-1} is not attributed to magnetic scattering disappearance.

RESULTS AND DISCUSSION

The phase transition makes the particles ensemble more homogeneous. Meanwhile, at $T \approx T_C$ an excess in scattering $\Delta I_{nC}/I_{nC} \sim 2\%$ testifies to the density fluctuations caused by fast spin diffusion. At high ferrite susceptibility ($T \approx T_C$) a ferroparticle can produce large-scale magnetic and density fluctuations. It polarizes the neighbors attracting them (like particles association in the external field). Near T_C a particle's moment reversal should be very quick ($\leq 10^{-9}$s) as compared to translational diffusion. Particle's shift ~ R_P takes a time $t_R \sim R_P^2/6D_S \sim 10^{-6}$s defined by the diffusion constant $D_S \sim 10^{-7}$cm^2/s. As we know [6], the ordering of a magnet means the spin cross section $d\sigma/d\Omega \propto r_C^3[1+(r_C q)^2]^{-1} \propto r_C(T)/q^2{}_{T \to Tc}$ growth as a radius $r_C(T)$ of the correlation of spins coupled by exchange forces. In FF the exchange vanishes at the borders of the cores, *i.e.,* the magnetic correlations in FF are created by dipole forces.

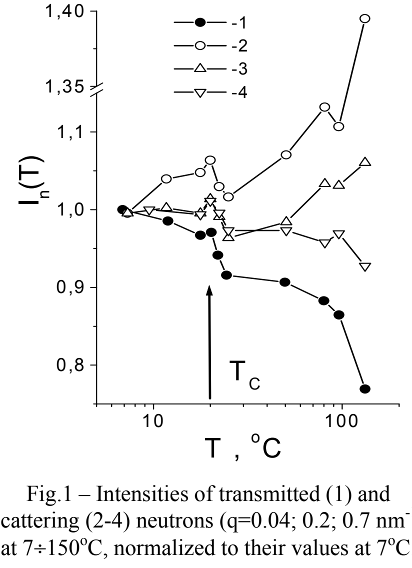

Fig.1 – Intensities of transmitted (1) and scattering (2-4) neutrons (q=0.04; 0.2; 0.7 nm^{-1}) at 7÷150°C, normalized to their values at 7°C.

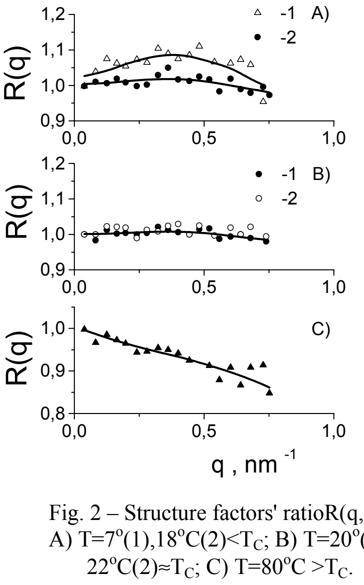

Fig. 2 – Structure factors' ratioR(q,T): A) T=7°(1),18°C(2)<T_C; B) T=20°(1), 22°C(2)≈T_C; C) T=80°C >T_C.

First we observed a full evolution: "super-paramagnet → paramagnet → surfactant shells' destruction → aggregation (Fig.1). In the first approximation the scattered intensities obey the law $I(q)=I_o[1+(qR_C)^2]^{-2}$ where the forward intensity $I_o(T)$ and the correlation radius $R_C(T)$ are temperature dependent and reflect mostly nuclear correlation which demonstrates an asymptotic behavior $I(q)\propto 1/q^4$, $(qR_C)^2>>1$. Note: the cross section of the magnetic fluctuations gives the contribution $\sim 1/q^2$ more pronounced at high q. In the range $7\le T\le 60^oC$ we found the correlation length $R_C\approx 2.4\text{-}2.5\text{nm} \approx$ const. It gives in spherical approximation the radius of the core $R_P=R_C\sqrt{10}\approx 8\text{nm}$ being close to light scattering data. The heating intensifies scattering ($T>100^oC$) as a result of the particles' inelastic collisions destroying shells and inciting aggregation to clusters (correlation length $R_C\sim 6\text{nm}$).

The intensities I(q,T), normalized to the values $I(q_{min},T_P)$ at $T_P=25^oC$ and $q_{min}=0.04\text{nm}^{-1}$, give the ratio of the structure factors (Fig. 2):

$$I_{NS}=I(q,T)/I(q,T_P)=S(q,T)/S(q,T_P)$$

and finally the functions $R(q,T)=I_{NS}(q,T)/I_{NS}(q_{min},T)$.

At $T_P = 25^oC > T_C$ dipole forces are negligible ($\sim 10^6$ weaker than at $T<T_C$). Therefore the R(q,T) reveals the structural features created by the dipole forces. The maximum of R(q,T) at $q_m\sim 0.3\text{-}0.4\text{nm}^{-1}$ corresponds to a particle diameter $D_P\sim 2\pi/q_m\sim 20$ nm that indicates their often contacts at $T<T_C$. The heating destroys the short-range order, and the maximum disappeared ($R(q) \approx$ const.). Above 50^oC the R(q) is increasing at $q\to 0$ that indicates an aggregation. At $T<T_C$ the constant $\Lambda=\mu^2/(k_BT\cdot D_P^3)\sim 1\cdot 10^{-2}$ of moments (μ) coupling is rather small as well as the association probability and the scattering intensity drop $(-\Delta I_n/I_n)\sim[1-\exp(-\Lambda)]\sim 10^{-2}$ by transition. These correlations are living at the characteristic time $t \le t_R\sim 10^{-6}$s of particles diffusion to length $\sim R_P$.

In order to find dynamic correlations we used dense FF ($T_C=20^oC$, C=15% vol.) in Neutron Spin Echo experiments (LLB, NSE "MESS", $\lambda=0.6$ nm). The temperature and the time-range were $T=8\div 57^oC$ and t=0-20 ns at momentum transfer $q=1\text{nm}^{-1}>R_P^{-1}$ which is larger than the reciprocal radius [3-6]. Thus, we observed the motion of single particles. The NSE-signal P(t,T) is decreasing as a function of time at $T<T_C$ and $T>T_C$. Near T_C it comes down drastically at small time $t\le 1$ ns. (Fig. 3). Its following changes are weaker than those observed out of the critical region. Because of $q>\pi/R_p$, we can neglect pair correlations considering the signal $P(t,T,q)=G_S(t,T,q)$ as a self-correlation function of the particle. In gaussian approximation $G_S(t,q)=\exp[-q^2\cdot\Gamma(t)/2]$ depends on the squared particle's displacement $\Gamma(t)$ along **q** for time t.

At the content C=15% the average distance between particles $R_{INC}=R_P(4\pi/3C)^{1/3} \sim 30\text{nm} \ge 2R_P\sim 20\text{nm}$ is larger than the diameter by the radius value, *i.e.,* particle's free diffusion is possible at lengths < R_P~10nm. Usually the diffusion shift $\Gamma(t)=r_o^2+2D_{ST}\cdot t$ is a linear function of time where r_o is the amplitude of fast particles vibrations and D_{ST} is the diffusion constant.

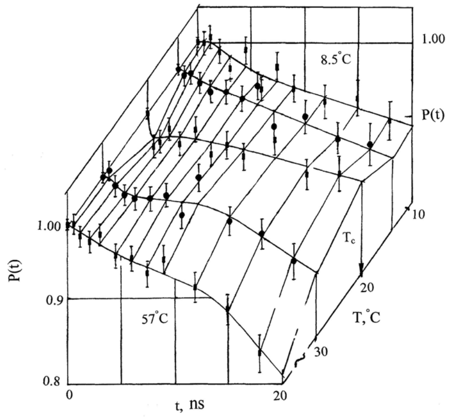

Fig. 3 – NSE-signal from FF *vs*. time and temperature, $q=1nm^{-1}$. Spline-functions are shown.

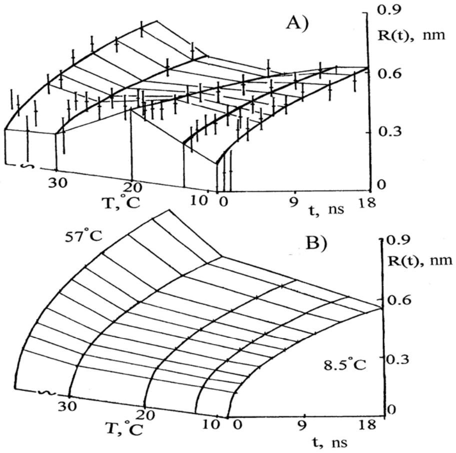

Fig. 4 – Measured (A) and calculated (B) shift for Stokes diffusion *vs*. time, temperature.

The measured $\Gamma(t)\leq 1nm$ obeys the function $\Gamma(t)=r_o^2+2D_F\cdot t$ with parameters $D_F(T)$, $r_o^2(T)$, but experimental shifts $R(t,T)=\Gamma(t,T)^{1/2}$ differ from the $R(t,T)=[2D_{ST}\cdot t]^{1/2}$ computed for Stokes diffusion. Here $D_{ST}=k_BT/(6\pi\cdot\eta\cdot R_h)$, $\eta(T)$ is medium viscosity $\eta(T)$, R_h is particle's hydrodynamic radius (Fig. 4). Below and above T_C the amplitudes $R(t\rightarrow 0)=r_o$~0.1-0.2 nm are at the same level, but near T_C the r_o~0.4 nm takes a doubled magnitude.

According to this, in the critical region the diffusion slows down by a factor of 2 as compared to the value out of the critical region (Fig. 5). Such a behavior of $D_F(T)$ is in contradiction with the free diffusion model. We observe that the magnetic critical fluctuations act anomalously on the particles' dynamics. The magnetic forces, blocking diffusion, generate high amplitude vibrations. In the diffusion process a particle needs free volume to be created by its neighbors regrouped. Meanwhile high rate vibrations increase effectively the particles' volumes. Hence, the total free volume, needed for particle jumping, decreases, and diffusion slows down. Despite of the low energy (~$10^{-2}k_BT$) the dipole forces create "fluctuating living chains" of the correlated moments due to anisotropy, long-range action and high critical susceptibility of the magnetic phase. These factors can cause anomalous diffusion damping in FF near T_C.

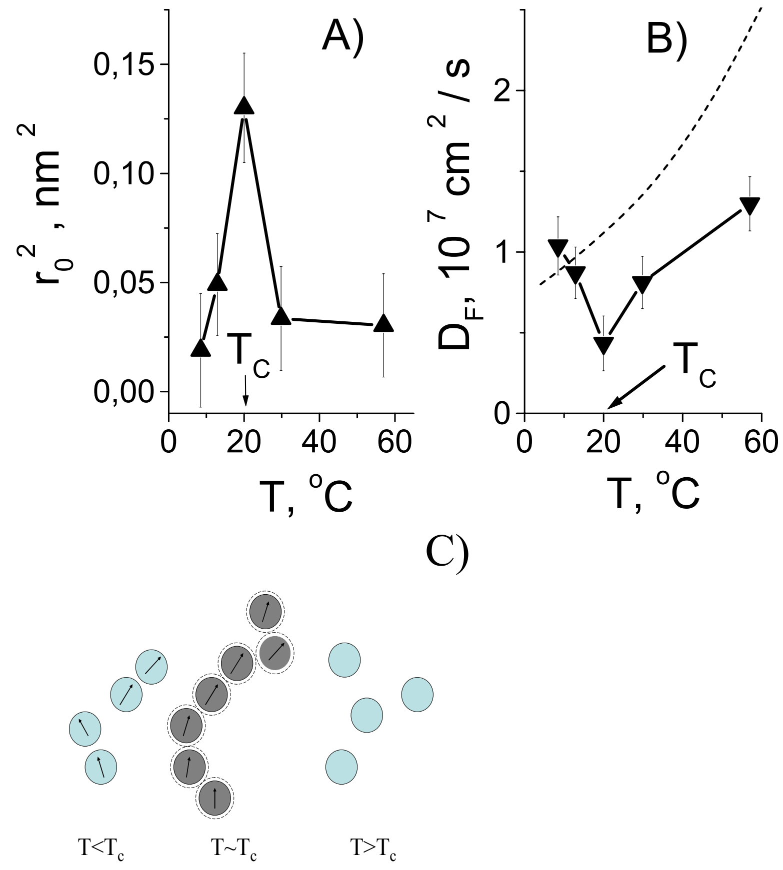

Fig.5. Dynamic parameters at T = 8-60°C:
A) squared vibrations amplitude $r_o^2(T)$; B) diffusion constant $D_F(T)$; dashed line shows free diffusion;
C) The schematic arrangement of particles.

CONCLUSION

Combining SANS and NSE methods we have studied the evolution of structure and dynamics of ferrofluid from super paramagnetic to critical and paramagnetic state. In this way there were separated correctly the static particles correlations (short-range order) induced by weak dipole interactions enforced sufficiently due to their anisotropy and long-range character. From inelastic neutron scattering in critical region we found the translational diffusion damping of the particles but their vibrational amplitudes incrérease at $T \approx T_C$ as compared to this one at $T < T_C$ and $T > T_C$.

The diffusion blocking at $T \approx T_C$ is in contradiction to free Stokes diffusion. The critical "freezing" of the ensemble of colloidal particles results from the high susceptibility of the magnetic phase. A given particle can polarize surrounding magnetic moments and attract them. Near a particle a probability of free volume formation needed for diffusion decreases. At the same time, fast moments fluctuations induce large-amplitude vibrations of the particles.

Our investigations of the ferrofluid structure and dynamics around T_C have shown a crucial role of the magnetic critical phenomena as defining the behavior of the colloidal system despite of the weak magnetic properties of the the magnetic phase.

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