ELSEVIER

Physica B 276–278 (2000) 396–397

PHYSICA B

www.elsevier.com/locate/physb

# NSE-study of magnetic phase dynamics in poly(vinylalcohol) ferrogel

Gy. Török[a,*], V.T. Lebedev[b], L. Cser[a], M. Zrinyi[c]

[a]*Research Institute for Solid State Physics, Konkoly Th. u. 29-33, P.O.B. 49, H-1525 Budapest, Hungary*
[b]*Petersburg Nuclear Physics Institute, 188350, Gatchina, St.-Petersburg distr., Russia*
[c]*Technical University of Budapest, H-1521, Budapest, Hungary*

**Abstract**

New magnetic field-sensitive hydrogels have been synthesized using cross-linked poly(vinylalcohol) with attached subdomain particles of $Fe_3O_4$ (size $\sim 100$ Å). The SANS experiments in field ($B \sim 3$ kG) have shown binding to the network of particles. No translational diffusion of $Fe_3O_4$ particles was observed. In ferrogel dynamics the stretched oscillating modes (frequency $\sim 10^8$ Hz) arising from fast Néel's fluctuations of particles magnetic moments dominate © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Magnetic colloid; Dynamics

Ferrogels (FG) are new materials with magnetic nanocrystals, embedded in a flexible polymer network, that provides their high magnetoelasticity whose property is to be applied in electronics and micromechanics [1]. Their anomalous behavior in magnetic field can be treated comprehensively in terms of microstructure and dynamics. We have investigated the FG composed of $Fe_3O_4$-subdomain particles (size $\sim 100$ Å, concentration $C = 4.25$ w%) associated with cross-linked poly(vinylalcohol) ($\sim$300 units between junctions). The SANS measurements in field ($B \sim 3$ kG) confirmed the localization of particles in polymer matrix. They did not show any redistribution as observed in other networks with free particles [2]. The neutron spin-echo measurements (carried out on MESS facility of LLB, Saclay) at momentum transfer $q_1 = 0.027$ Å$^{-1}$ and $q_2 = 0.037$ Å$^{-1}$ which is higher than the inverse value of particles size $1/R_p$. At this $q$-scale we expected the domination of self-correlation in scattering. To elucidate the dynamics of particles in network, we have examined also the ferrofluids (FF) ($C_1 = 6.0$ w% and $C_2 = 1.5$ w%), containing the same (free) particles as the gel.

In all cases without external field (Figs. 1 and 2) we found that the time-dependent correlation function

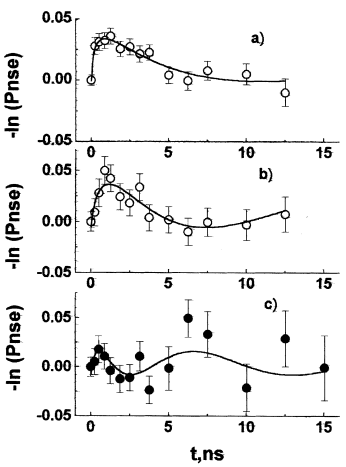


Fig. 1. NSE-signal at $q_1 = 0.027$ Å$^{-1}$ from FF1 (a), FF2(b) at $T = 293$ K and FG(c) at $T = 343$ K. Line shows the fitting by model function (Table 1).

*Corresponding author. Tel.: +36-1-169-9499; fax: +36-1-169-7128.
*E-mail address:* torok@power.szfki.kfki.hu (Gy. Török)

0921-4526/00/$ - see front matter 
PII: S0921-4526(99)01593-8

Table 1
Dynamic parameters at $q_1 = 0.027$ Å$^{-1}$

| Sample | C (w%) | Temperature (K) | $d$ (Å) | $\omega$ (1/ns$^{\beta}$) | $\beta$ |
|---|---|---|---|---|---|
| FF concentrated | 6.0 | 293 | $9.6 \pm 0.7$ | $3.26 \pm 0.27$ | $0.27 \pm 0.06$ |
| FF diluted | 1.5 | 293 | $10.6 \pm 1.2$ | $2.96 \pm 0.34$ | $0.37 \pm 0.06$ |
| FG | 4.25 | 343 | $7.9 \pm 1.7$ | $4.21 \pm 0.66$ | $0.43 \pm 0.09$ |

Table 2
Dynamic parameters at $q_2 = 0.037$ Å$^{-1}$

| Sample | C (w%) | Temperature (K) | $d$ (Å) | $\omega$ (1/ns$^{\beta}$) | $\beta$ |
|---|---|---|---|---|---|
| FF concentrated | 6.0 | 293 | $7.0 \pm 0.9$ | $2.22 \pm 0.41$ | $0.53 \pm 0.16$ |
| FF diluted | 1.5 | 293 | $5.1 \pm 2.3$ | $0.40 \pm 0.84$ | $1.16 \pm 1.00$ |

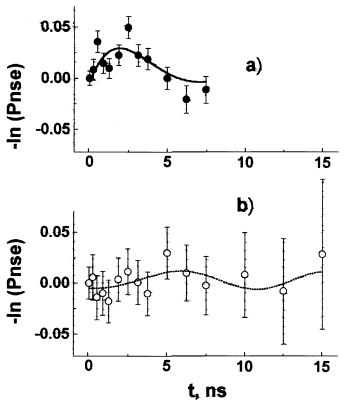


Fig. 2. NSE-signal at $q_2 = 0.037$ Å$^{-1}$ from FF1(a) and FF2(b) at $T = 293$ K. Line is the approximation by model function (Table 2).

(NSE-signal): $P_{\mathrm{NSE}} = S(q,t)/S(q,0) \cong 1 - q^2 r^2(t)/2$ (the $r^2(t)$ is the squared particle's displacement) possesses stretched oscillating behavior. For Stokes diffusion one can expect $r^2(t) \sim t$. In reality, the anisotropic long-range dipole interactions induce various relaxation processes in the ensemble of particles, demonstrating the motion with $r^2(t) = d^2\{1 - \cos[\varphi(t)]\}/2$ where $d$ is the amplitude and $\varphi(t) = \omega t^{\beta}$ is the phase of oscillations (the model of oscillator with frequency $\omega$ at $\beta = 1$). This model describes the data satisfactory. The parameters obtained by fit are given in Tables 1 and 2. The concentrated FF shows a very stretched relaxation at lower $q = q_1$, whereas at $q_2 > q_1$ the exponent $\beta$ is greater. In polymers stretched relaxation (no oscillations, $\beta \sim 0.4$) was observed [3].

The dynamics of FF and FG exhibits the motion of chain-like structures composed of random dipole "bonds" between particles. The magnitudes of $\beta$ in diluted FF and FG are comparable. The higher "frequency" in FG results from the network's contribution to particles' interaction (Table 1). The amplitude of motion $d \sim 10$ Å in ferrofluids at ambient temperature has the same order as in ferrogel at significantly higher temperature. At ambient temperature the gel dynamics is damped. At $T \sim 343$ K the network (highly elastic) does not restrict the local motion of attached particles but influence to the rate and character of their motion. This observation gave the evidence of the existence of similar oscillating modes in FF and FG due to magnetic interaction of nanoparticles. In all systems the effective frequency $\omega \sim 2\pi/\tau_0^{\beta}$ is determined by characteristic time $\tau_0 = 6.1 \pm 2.5$ ns associated with fast fluctuations of magnetic moments inside particles (Néel's relaxation).

We are very grateful to Drs. A. Brulet and Gy. Kali, I.N. Ivanova and S.M. Bogdanovich for assistance. The research was supported by Russian Min. of Sci. (pr."Uporyadochenie", "Neutron Res. of Condensed Matter"), Russ. Fund for Basic Res. (gr.L-EN-96-15-96775) and Hungarian Research Found (OTKA,Grant T-017016).

## References

[1] M. Zrinyi, L. Barsi, A. Buki, J. Chem. Phys. 104 (1996) 8750.
[2] V.T. Lebedev, Gy. Torok, L. Cser, A.L. Buyanov, L.G. Revelskaya, D.N. Orlova, A.I. Sibilev, J. Magn. Magn. Mater. 201 (1999) 136.
[3] B. Frick, D. Richter, in: D. Richter, A.J. Dianoux, W. Petry, J. Teixeira (Eds.), Springer Proceedings in Physics, Vol. 37, Springer, Berlin, 1989, pp. 38–52.