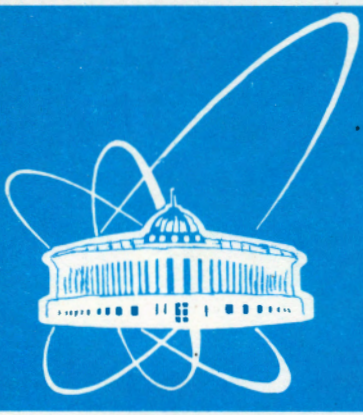

СООБЩЕНИЯ
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APPLICATION OF CONTRAST VARIATION METHOD IN SANS EXPERIMENTS WITH FERROFLUIDS

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1 Introduction

The contrast variation method has been largely used over the years in small angle scattering experiments to study the structure of multicomponent systems. For ferrofluids, it was applied by Ccbula, Charles and Popplewell [1]. However, the magnetic contribution to the counting rate was estimated by these authors from the magnetic volume fraction of the sample, as obtained by the magnetization measurements.

The possibility to simultaneously obtain information about both the magnetic and molccular structure of ferrofluids, by means of contrast variation method, in a SANS experiment, was considered in a previous paper [2]. There it was shown that the separate determination of the contribution to scattering pattern of nuclear and magnetic interactions may be accomplished even with unpolarized neutrons, *i.e.* in the absence of any perturbation produced by an external magnetic field, otherwise involved in the usual methods with polarized beams. To the preliminary results reported in [2] the present ones, obtained on a new series of similar samples, by the samc methods but with an improved cxperimental statistics, are added. Moreover, the limitations caused by the size polydispersity of the particles are considered herewith in detail and sources of further improvements of the method are identified.

2. Basic concept

In a SANS experiment with ferrofluids, the excess scattering power of the colloidal particles, $I(Q)$, is defined as the difference between $I_s(Q)$ - the counting rate produced by magnctic liquid and $I_c(Q)$ - the counting rate corresponding to the carrier liquid free of particles. Q is the momentum transfer, $Q = (4\pi/\lambda)\sin(\theta/2)$, where λ is the neutron wavelength while θ is the scattering angle. For diluted solutions of nearly spherical particles, neglecting the size polydispersity, the function I(Q) corresponding to the scattering of unpolarized neutrons, in the Guinier's Q-range, may be expressed as:

$$I(Q) = I_n(0)\exp(-Q^2R_{gn}^2/3) + I_m(0)\exp(-Q^2R_{gm}^2/3) \qquad (1)$$

where R_{gn} and R_{gm} are the *nuclear* and *magnetic* gyration radii while:

$$I_n(0) = k\,(f^*)^2\,V_d^2 \qquad (2)$$

$$I_m(0) = (2/3)\,k\,f_m^2\,V_m^2 \qquad (3)$$

are referring to the nuclear and magnetic scattering. In the above formulae:

k is a constant containing the particles density and absolute scattering factors; V_d is the effective volume of the particle excluded from the carrier liquid; f^* is the *nuclear contrast* (i.e. the overall excess scattering density, $f(\mathbf{r})$, due to the particle above that of the carrier liquid, f_s,) defined as:

$$f^* = \frac{1}{V_d}\int (f(\mathbf{r}) - f_s)d\mathbf{r} = \frac{R_c^3(f_c - f_s) + [\Phi f_a - (1-\gamma)f_s][(R_c+t)^3 - R_c^3]}{R_t^3 - \gamma[(R_c+t)^3 - R_c^3]} \qquad (4)$$

R_c is the radius of magnetite core and t is the thickness of surfactant layer; $V_s = (4\pi/3)[(R_c+t)^3 - R_c^3]$ the volume of the external layer from which ϕ is the volume fraction of the surfactant and γ is the volume fraction of the carrier; f_c and f_a are the nuclear scattering densities of the magnetic core and of the surfactant; f_m is the magnetic scattering density while V_m is the magnetic effective volume of the particle.

By using mixtures of H- and D- carrier liquids, with x-the volume fraction of the latter, the scattering density of the carrier, $f_s = (1-x)f_H + xf_D$, may be varied between f_H and f_D, the values corresponding to pure components. Consequently, the *nuclear contrast*, f^*, varies drastically and in this way one can investigate $f(\mathbf{r})$ obtaining information about the colloidal particle structure. Moreover, for a certain value x_0 one may obtain $f^*(x_0) = 0$ so that for this concentration $I_n(0, x_0) = 0$ and the measured intensity may be entirely attributed to the magnetic scattering which is not dependent on x. Therefore, generally, one may write:

$$I_m(Q) = I(Q, x_0) \qquad (5)$$

$$I_n(Q, x) = I(Q, x) - I(Q, x_0) \qquad (6)$$

3. Polydispersity

A log-normal distribution function of magnetite particle sizes R is considered:

$$D(R) = (1/\sigma\sqrt{2\pi})(1/R)\exp(-(\ln R - \ln R_0)^2/2\sigma^2).$$

The average of $I_n(0, x)$ over such a distribution may be expressed as:

$$\overline{I_n(0,x)} = Ax^2 + Bx + C \qquad (7)$$

where:

$$A = (a+b+c)(f_D - f_H)^2$$

$$B = [2(a+b+c)f_H - f_c(2a+c)](f_D - f_H) \qquad (8)$$

$$C = (a+b+c)f_H^2 + af_c^2 - f_c f_H(2a+c)$$

$$a = R_c^6 \exp(18\sigma^2)$$

$$b = (1-\gamma)^2 t^2 (9R_c^4 \exp(8\sigma^2) + 18t\,R_c^3 \exp(9\sigma^2/2) + 15t^2 R_c^2 \exp(2\sigma^2) + 6t^3 R_c \exp(\sigma^2/2) + t^4)$$

$$c = 2(1-\gamma)t(3R_c^5 \exp(25\sigma^2/2) + 3t\,R_c^4 \exp(8\sigma^2) + t^2 R_c^3 \exp(9\sigma^2/2).$$

An analysis of Eqs. (7) and (8) reveals that a positive minimum always appears for $x_0 = -B/2A$ and that its magnitude is:

$$\overline{I_n(0,x_0)} = (4AC - B^2)/4A. \qquad (9)$$

This value is equal to zero only for $\sigma = 0$, otherwise only for mono-sized particles. However, a limiting value σ_0 may be found, under which $\overline{I_n(0,x_0)}$ takes negligible values, smaller than the statistical experimental errors, so that the approximation $\overline{I_n(0,x_0)} \approx 0$ is acceptable.

4. Experimental results

The experiments were done on a new series of magnetite ferrofluids ($f_c = 6.977 \cdot 10^{10}\,cm^{-2}$) with oleic acid surfactant ($f_a = 0.077 \cdot 10^{10}\,cm^{-2}$) and benzene carrier ($f_H = 1.182 \cdot 10^{10}\,cm^{-2}$ and $f_D = 5.437 \cdot 10^{10}\,cm^{-2}$). The average magnitude of the magnetite particle, obtained by electron microscopy (EM), was R_c=47 A with a standard deviation

$\sigma_0 \approx 0.08$. The D- benzene volume fraction was produced to take seven different values: x=0; 0.2; 0.5; 0.6; 0.7; 0.8 and 1.0. The overall volume fraction of the magnetite particles was 0.6%. The measurements were performed with the small angle scattering facility IUMO (MURN) in operation at the IBR-2 pulsed reactor of the JINR-Dubna [3].

Like with the preliminary experiments [2], $I(0,x)$, the extrapolation of the total intensity to $Q = 0$, exhibits a minimum in the vicinity of $x \approx 0.6$, approximately indicating the point where f^* changes its sign and, by means of Eqs.(5) and (6), allowing to find out the *nuclear* and *magnetic* intensities, $I_n(Q,x)$ and $I_m(Q,x)$.

The Guinier plots $\ln(I_n(Q,x))$ vs. Q^2 are shown in Fig.1 for different values of x. From the best straight line fits of these, $I_n(0,x)$ and $R_{gn}^2(x)$ were obtained. On the basis of Eq.(2), a subsequent straight line fit of $[I_n(0,x)]^{1/2}$ vs. x, illustrated in Fig.2, gives the following values of the structural parameters of colloidal particle: $R_c = 46 \pm 1.8$ Å, $t = 18.7 \pm 0.6$ Å, $\gamma = 0.532 \pm 0.15$. At the same time the value $k = 7.74 \cdot 10^8\ cm^{-3}$ is found. The small value of the oleic acid scattering amplitude prevents the determination of the surfactant volume fraction ϕ.

Fig.3 represents a plot of $R_{gn}^2(x)$ against $1/f^*$. A linear dependence, predicted in [1], is evidenced. However, only the points corresponding to those values of x where the scattered intensity is sufficiently high, being far enough from the *reversing point* x_0, are shown.

With the measured values of structural parameters, accordingly to Eq.(9), at $x_0 = 0.6$ a standard deviation $\sigma_0 \approx 0.1$ ensures a value of the nuclear intensity representing less than 5% from the total measured intensity. Because the experimental error is also about 5% one can conclude that the effect of polydispersity cannot be distinguished and the entire scattering intensity could be assigned to the magnetic scattering.

A Guinier plot of $\ln(I_m(Q,x_0))$ vs. Q^2 gives, also by linear best squares fitting, the magnitudes of $I_m(0,x_0)$ and $R_{gm}^2(x_0)$. Consequently one obtains the *effective magnetic radius* of the magnetite core $R_m = (5/3)^{1/2} R_{gm} = 36 \pm 1.8$ Å while for the magnetic scattering density $f_m = (2.775 \pm 0.18) \cdot 10^{10}\ cm^{-2}$ is found.

By taking into account the same law to define the polydispersity of magnetic volumes, an average magnetic volume $\overline{V_m} = \exp(9\sigma_0^2/2)\ V_m \approx 1.03\, V_m$ is obtained.

5. Discussion

Different from the preliminary measurements [2] in which the magnetic core radius R_c obtained by EM measurements and the literature data referring to the length of the oleic acid molecule ($t \approx 20$ Å) were considered as input data, this time, the increased experimental statistics made possible to derive the magnitudes of these entities by SANS experimental data. However, the magnitude of R_c is in a good agreement with the mean value determined by EM for the present samples while the obtained value of t represents a satisfactory result, as well. A *dry volume* of colloidal particle $V_d = (4.07 \pm 0.16) \cdot 10^5\ Å^3$ was found.

As concerns the magnetic scattering, now both V_m and f_m were measured. Anyway, the actual value of f_m does not differ too much from the previously used magnitude $f_m = 3.068 \cdot 10^{10}\ cm^{-2}$ derived from macroscopic measurements [4].

More information concerning the interaction of surfactant with the particle surface and the role played by the carrier in penetrating the surfactant layer, could be obtained with further experiments provided that the accuracy of the data should be increased. Besides the reduction of experimental errors, the number of samples with different D/H- ratio of the carrier should be increased. More such points are necessary in the neighborhood of the reversion point, for a precise determination of it. However, about x_0 the nuclear intensity takes small or even vanishing values and the gyration radii are not well defined so that the measurements have to be

equally done in as many as possible points in all [0-1] x- interval, to say nothing about their position relative to x_0.

A pronounced size polydispersity may hinder accurate structural measurements. However, a limiting value $\sigma_0 \approx 0.1$ seems to be usual for many classes of ferrofluids (prepared by different methods) as shown by O'Grady and Bradbury [5].

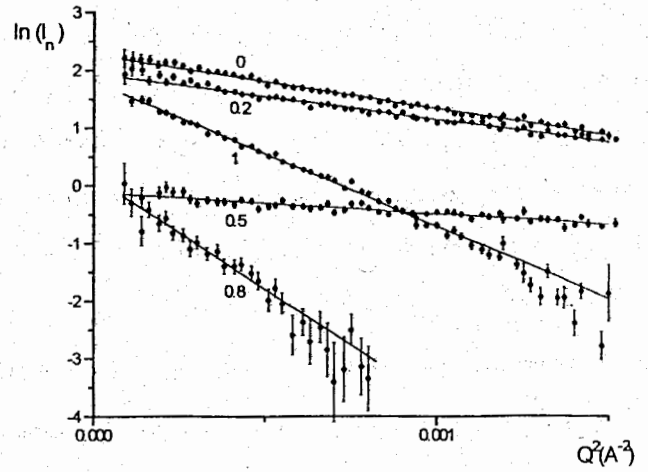

Fig.1 The Guinier plots of $\ln(I_n(Q,x))$ vs. Q^2 for several values of x (0; 0.2; 0.5; 0.8 and 1.0). Good straight lines are evident.

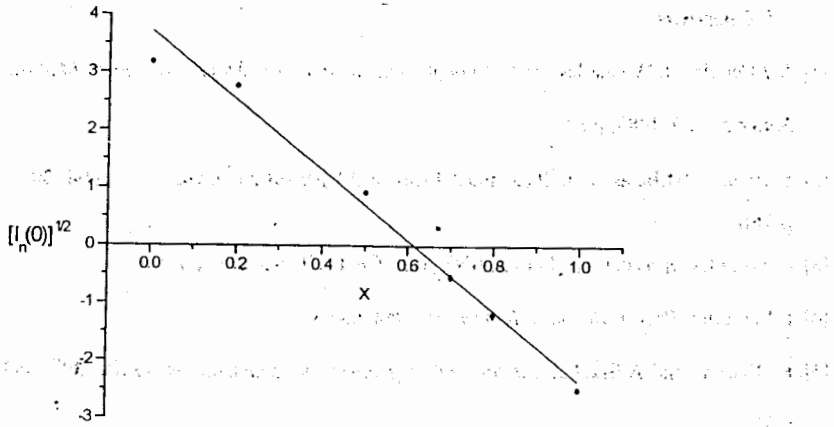

Fig.2 The plot $\sqrt{I_n(0,x)}$ against x. The reversing point, from which $I_n(0,x)=0$, is seen in the vicinity of $x = 0.6$.

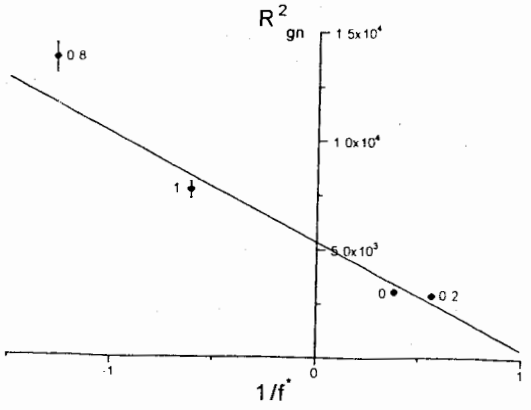

Fig.3 $R_{gn}^2(x)$ against $1/f^*$. A linear dependence is evident. The values of x placed in the neighborhood of x_0 are not taken into consideration because in these points the nuclear scattering intensity takes small values hindering the accurate determination of gyration radii.

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Применение контрастного вариационного метода
в эксперименте по малоугловому нейтронному рассеянию
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Контрастный вариационный метод, примененный в эксперименте по малоугловому нейтронному рассеянию, был использован для одновременного получения информации о молекулярной и магнитной структурах феррожидкостей. Рассмотрены ограничения, обусловленные полидисперсностью частиц.

Работа выполнена в Лаборатории нейтронной физики им. И.М.Франка ОИЯИ.

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