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Physics Abstracts

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Magnetic anisotropy of ferrosmectic phases

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Résumé. — Un nouveau fluide magnétique anisotrope, appelé ferrosmectique, est obtenu lorsque nous utilisons un ferrofluide, c'est-à-dire une suspension colloïdale de particules magnétiques de taille inférieure au micron, comme composant dans la fabrication d'une phase smectique de membranes fluides. Ces phases adoptent des comportements spécifiques sous champ magnétique, et nous présentons ici une étude de l'anisotropie de leur susceptibilité magnétique en fonction de la concentration en particules. Nous interprétons les résultats obtenus par un mécanisme microscopique basé sur l'existence d'une gêne stérique entre membranes et particules.

Abstract. — A new anisotropic magnetic fluid, called ferrosmectic, is obtained when using a colloidal suspension of submicronic magnetic particles (ferrofluid), as a component in a smectic phase of fluid membranes. These lamellar phases present specific magnetic properties. The anisotropy of their magnetic susceptibilities as a function of particles concentration is studied and interpreted: a microscopic mechanism involving a steric hindrance between particles and membranes is used to understand the experimental results.

Introduction.

Ferrosmectic phases are hybrid systems constituted of layers of organic ferrofluid separated by surfactant sheets: they are obtained by dispersing ferrimagnetic particles into a lyotropic lamellar phase [1, 2]. Recent studies of the structure of these phases by small-angle neutron scattering [3] and of their hydrodynamic modes by quasi-elastic light scattering [4] have demonstrated the existence of interactions between solid particles and fluid membranes in a ferrosmectic phase [5]. One of the most striking consequences of this coupling between particles and membranes is observed in the very specific response of ferrosmectic samples to a weak magnetic field [1, 6]. This behavior may be summarized as follows: when an external field larger than a threshold of a few tens of Oersted is applied perpendicularly to the layers of

an oriented ferrosmectic, instabilities corresponding to a rotation of the lyotropic structure develop, leading to a reorientation of the lamellae parallel to the field. The rotation of the structure in the field shows that ferrosmectic phases possess a magnetic anisotropy which is related to the layering of the system, and that their lining up parallel to the field is energetically favored.

In order to interpret this instability, the magnetic anisotropy of the system and its variation with the relevant parameters have to be determined, as well as the magnetic properties of the constituent ferrofluid. A ferrofluid suspension is an isotropic superparamagnetic medium described by a scalar susceptibility χ but, once this suspension incorporated into a smectic phase, the magnetic properties of the anisotropic system have to be described by a tensor of susceptibility. The ferrosmectic being a uniaxial material, two numbers are sufficient for its characterization and the tensor of susceptibility can be written as :

$$\tilde{\chi} = \begin{pmatrix} \chi_{\perp} & 0 & 0 \\ 0 & \chi_{\parallel} & 0 \\ 0 & 0 & \chi_{\parallel} \end{pmatrix}$$

where χ_{\parallel} is the susceptibility parallel to the lamellae, and χ_{\perp} the perpendicular one. The magnetic anisotropy is measured by the value of the anisotropy of susceptibility :

$$\chi_a = \chi_{\perp} - \chi_{\parallel} .$$

In the following, we present measurements of the susceptibilities χ_{\parallel} and χ_{\perp} of the ferrosmectic as a function of the particle volume fraction. The experiments have been performed with oriented samples, in two different geometries. We have to underline that the orientation of these liquid samples is fragile towards flow or magnetic field : this happened to be a major difficulty in our experiments.

1. Sample characteristics.

1.1 FERROFLUID. — The colloidal particles are made of a ferrimagnetic iron oxide (maghemite) characterized by a bulk magnetization $M_s = 3.8 \times 10^5 \text{ A} \cdot \text{m}^{-1}$. They are small enough to be magnetic monodomains and thus bear a permanent moment $m = M_s v$, where v is the volume of the particles. These particles are dispersed in cyclohexane, where they are stabilized by a shell of surfactant molecules physisorbed on their surface. The volume v and, in the following, the diameter D refer to the solid core of the particles, and do not take the surfactant shell into account. The particle volume fraction is of the order of a few percents. In zero magnetic field, the colloidal suspension exhibits no magnetization because of thermal motion. When an external field is applied, the particle moments align parallel to the field either by Brownian rotation (the whole particle rotates in the surrounding fluid) or by Néel relaxation (the magnetization direction changes with respect to the crystalline structure of the particle) [7, 8]. Both mechanisms lead to a ferrofluid magnetization curve that follows a Langevin paramagnetism behavior : the ferrofluid is said to be superparamagnetic. The superparamagnetic susceptibility χ , given by the initial slope of the law $M(H)$, is proportional to the particle volume fraction.

1.2 FERROSMECTIC PHASES. — Ferrosmectic phases are obtained by combining two colloidal systems : the first one is the ferrofluid described above, and the second one a quaternary lamellar phase water-sodium dodecylsulphate-pentanol-cyclohexane. The lamellar phase is composed of membranes of amphiphilic molecules and water, of constant thickness 5 nm, organized with a smectic order in a cyclohexane solvent. In the case of a ferrosmectic, the

cyclohexane solvent is replaced by ferrofluid: the parameter characterizing the amount of solvent (ferrofluid in this case) is called « swelling ratio » and is defined by $\Phi_s = \frac{\text{ferrofluid volume}}{\text{membrane volume}}$. It is equivalent to define the lamellar periodicity d , which is equal to the ferrofluid layer thickness plus the membrane thickness. The last relevant parameter describing this layered and doped system is the particle volume fraction φ . In order to compare ferrosmectic and ferrofluid samples, the particle volume fraction φ is defined as the ratio of the particle volume to the total volume of the smectic sample.

The samples used for these measurements are ferrosmectic phases with a periodicity ranging between 200 and 400 Å, and whose volume fractions in particles range between 0.004 and 0.03. We also measure for comparison the susceptibility of isotropic ferrofluid samples of volume fraction 0.011 and 0.023.

1.3 SAMPLE ORIENTATION. — The ferrosmectic phase is a uniaxial medium, which spontaneously tends to align in capillaries because of the existence of an anisotropic anchoring energy on glass walls. Two different configurations are obtained, according to the shape of the container, which are easily recognizable by observation under a polarizing microscope.

When the sample is placed in a capillary of rectangular cross-section (cf. Fig. 1), the anchoring conditions are favorable to a so-called *homeotropic* orientation in which the lamellae are parallel to the walls. When the cross-section of the capillary is square or has a small aspect ratio, homeotropic anchoring is no longer favored and the sample presents a *planar*

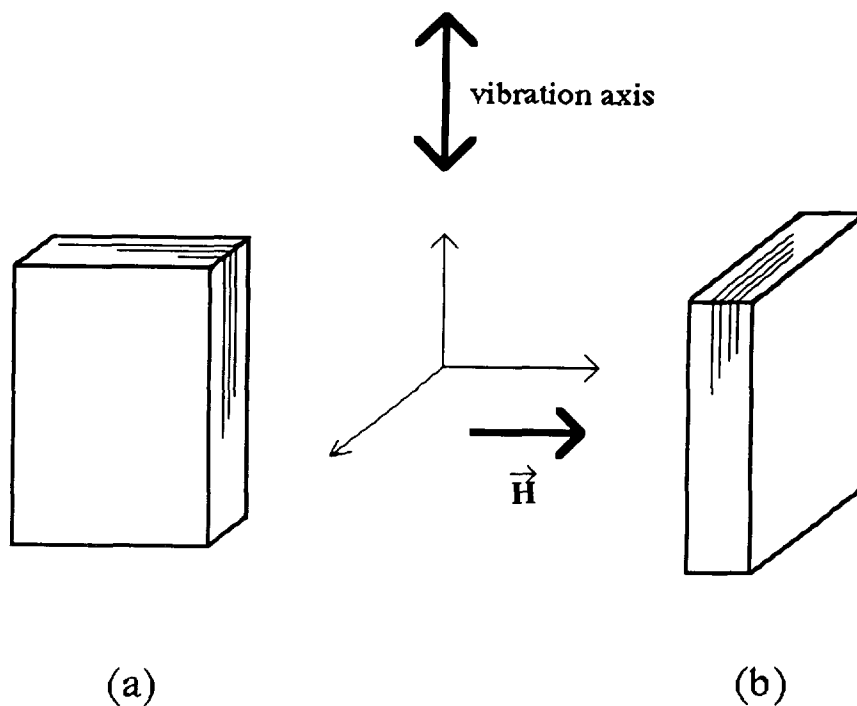


Fig. 1. — Geometry of the vibrating device experiments: parallel (a) and perpendicular (b) configurations are both obtained with a *homeotropic* orientation of the smectic in the rectangular capillary (the lamellae orientation is drawn in thin lines).

orientation, in which the lamellae are perpendicular to the glass walls and to the axis of the capillary (cf. Fig. 2a).

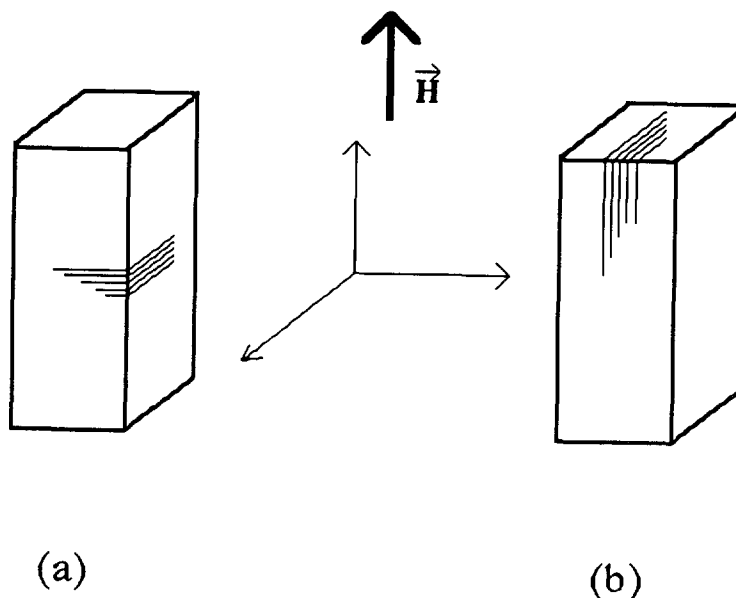


Fig. 2 — Geometry of the Squid experiments : the perpendicular configuration (a) is obtained when the smectic presents a *planar* orientation in the square capillary. The parallel configuration is represented in (b).

In the following experiments, sample orientation has been enhanced when needed, either by a thermal treatment, or by the action of an external magnetic field prior to the measurement. This will be specified in the description of each experiment.

1.4 DEMAGNETIZING FIELD OF THE SAMPLES. — As was mentioned above, the glass capillaries containing the ferrosmectic phases may present a non-negligible shape anisotropy. This shape anisotropy is responsible for a demagnetizing field effect which is superimposed to the intrinsic anisotropy of the fluid. With the (crude) assumption that the magnetization is homogeneous throughout the sample, one can use the relation between the intrinsic susceptibility χ_i and the measured susceptibility χ_s to derive χ_i :

$$\chi_i = \frac{\chi_s}{1 - \chi_s D}$$

In this relation, D is the demagnetizing factor :

$$D = \frac{2}{\pi} \operatorname{Arctg} \left(\frac{h\ell}{t \sqrt{\ell^2 + h^2 + t^2}} \right),$$

where h , ℓ and t are the three dimensions of the sample, t corresponding to the dimension in the field direction. This correction is systematically taken into account in the following, so that the results given in the third paragraph correspond to intrinsic susceptibilities.

2. Magnetic measurements.

Two experimental methods have been used which both present advantages and drawbacks.

2.1 MEASUREMENTS WITH THE VIBRATING SAMPLE DEVICE. — These measurements were carried out thanks to the kind hospitality of Dr. Philippe Monod, at the Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France.

The ferrosmectic samples are held in sealed capillaries of rectangular cross section 0.2×2 mm, in which the spontaneous homeotropic orientation has been enhanced by thermal annealing. The general principle of the experiment is as follows : the sample is placed between two polar pieces of an electromagnet and submitted to a horizontal external field \mathbf{H}_{ext} , it is vibrating vertically, i.e. perpendicularly to the field \mathbf{H}_{ext} , with a frequency $f = 50$ Hz, and an amplitude of a few centimeters. The value of the magnetization M of the sample is obtained from the component of the electromotive force induced at the same frequency f in two coils surrounding the sample. The parallel or perpendicular configurations are obtained by rotating the capillary around its axis (cf. Fig. 1).

Varying the external field H_{ext} between zero and a few tens of Oersteds, we plot the sample magnetization M as a function of H_{ext} . For all the phases studied, which are superparamagnetic, the plots exhibit a linear part for small fields, whose slope is the susceptibility of the sample.

A quasi-perfect homeotropic orientation is achieved in our capillaries, but the vibration of the sample may induce shear fields inside the capillary and build up defects. In these disoriented regions, the anisotropic properties are averaged so that we can only be sure to measure a value smaller than $|\chi_{\perp}|$. In order to avoid this problem, we have undertaken experiments with a device handling the sample more smoothly.

2.2 MEASUREMENTS WITH THE SQUID DEVICE. — A commercial SQUID magnetometer (Quantum Design Inc.) equipped with a superconducting magnet was used to measure the sample magnetization for discrete values of the field ranging between 0 and 40 Oe. The measurement process is smoother than previously but the geometry of the experiment is less favorable : because of reduced available space inside the magnetometer, the capillary can only be positioned with its main axis parallel to the field. This implies that, in order to measure both χ_{\perp} and χ_{\parallel} — which means to have the layers either parallel or perpendicular to the field —, one has to be able to produce two different orientations of the layers with respect to the capillary. As it is important for the measurements to be performed on the same sample, we have chosen to use capillaries with a square cross-section 1×1 mm, for which the spontaneous orientation of the lamellae is perpendicular to the capillary axis. This so-called planar initial orientation is enhanced by the action of a rotating magnetic field ($\sim 10^4$ G). In order to obtain the other configuration, we apply a strong field along the capillary axis, which reorients the lamellae parallel to it (cf. Fig. 2). We have checked that there is no relaxation towards the spontaneous planar orientation on the time scale of the measurements. Moreover, the effect of the demagnetizing field due to the shape anisotropy of the capillary is negligible in this case.

One disadvantage of this method is the existence of defect regions along the edges of the capillary due to defavorable anchoring conditions on the glass walls : once again, we can only be sure to measure a value smaller or equal to $|\chi_{\perp}|$.

3. Results.

The two sets of experiments give consistent results : however, the measurements made with the SQUID device show better experimental accuracy.

In a first step, we measure the magnetization of the bulk isotropic ferrofluid. The susceptibility χ_0 is obtained from the initial slope of the curve $M(H)$: in the present

concentration range it is, is expected, proportional to the volume fraction in particles and we obtain $\chi_0 = \alpha_0 \varphi$, with $\alpha_0 = 13.3$.

In the case of ferromagnetic samples, the plot of M_{\parallel} versus H_{ext} is also of a Langevin-type and its linear part allows the determination of χ_{\parallel} . From the magnetization curve M_{\perp} , we deduce in a similar way χ_{\perp} which is always smaller than χ_{\parallel} . However, in this case, a change of slope takes place: this second regime occurs for a field corresponding to the threshold of reorientation of the lamellae parallel to the field. The slope is different because the susceptibility measured above this value is now a combination between χ_{\perp} and χ_{\parallel} .

From the two susceptibilities, we deduce the value of $\chi_d = \chi_{\perp} - \chi_{\parallel}$. The measurements have been made for a whole set of samples, varying two parameters: the lamellar periodicity d and the particle volume fraction φ . For all the samples, χ_d is negative and its relative value $\frac{|\chi_d|}{\chi_{\parallel}}$ is constant and equal to 13 %.

More precisely, the characteristics of the susceptibilities χ_{\perp} and χ_{\parallel} are the following:

i) Evolution of the susceptibilities with the particle volume fraction φ .

The measurements of χ_{\perp} and χ_{\parallel} versus φ are plotted at constant swelling ratio. Both the parallel and perpendicular susceptibilities exhibit a linear variation with the volume fraction φ in the explored range (cf. Fig. 3); the slopes of these plots will be called α_{\parallel} and α_{\perp} . $\chi_{\parallel} = \alpha_{\parallel} \varphi$ and $\chi_{\perp} = \alpha_{\perp} \varphi$.

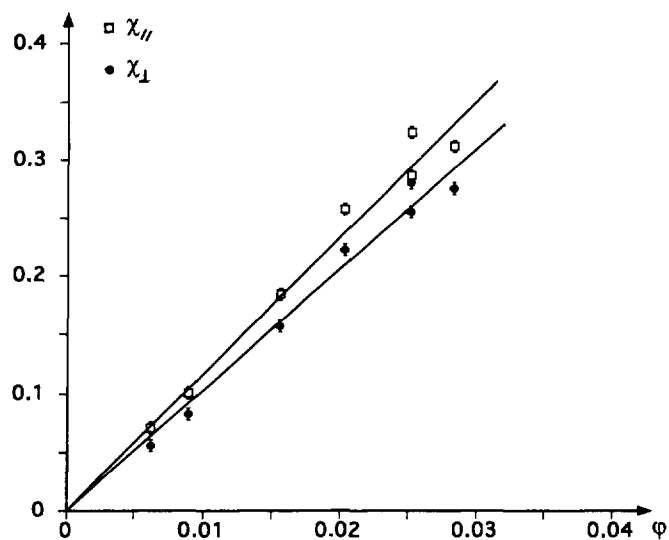


Fig. 3. — Evolution of the parallel and perpendicular susceptibilities (SQUID measurements) for ferromagnetic phases of volume fraction in particles increasing from 0.006 to 0.03 and for a constant swelling ratio $\Phi_s = 3.6$.

ii) Effect of the lamellar periodicity d .

We have investigated the variation of the susceptibilities with the swelling ratio, or equivalently with the lamellar periodicity d of the ferromagnetic phases. We summarize the evolution of the $\chi_{\perp}(\varphi)$ when the periodicity is varied by plotting in figure 4, the values of the slopes α_{\parallel} and α_{\perp} versus d . We observe that α_{\perp} slightly increases with d , whereas

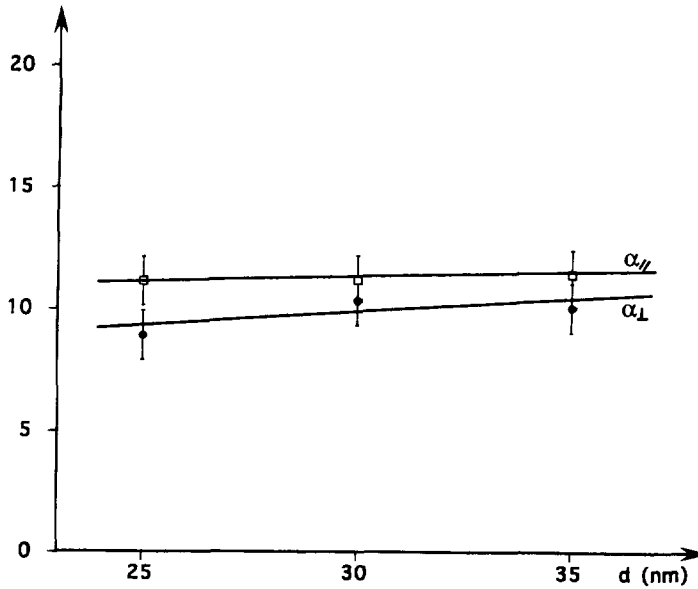


Fig. 4. — Evolution of the parallel and perpendicular slopes α_i of the $\chi_i(\varphi)$ plots (SQUID measurements) for ferrosmectic phases as a function of the periodicity d

α_{\parallel} remains almost constant. This corresponds to a slight decrease of χ_{\perp} with d , of the order of the experimental accuracy.

We will come back to this small variation with d later; but neglecting it in a first approximation, we plot the values of χ_{\parallel} and χ_{\perp} as a function of φ for the whole set of samples studied. The slopes of the $\chi_i(\varphi)$ plots are: $\alpha_{\parallel} = 11.8$ and $\alpha_{\perp} = 10.3$. The corresponding $\chi_{\perp}(\varphi)$ plot is given in figure 5.

4. Discussion.

4.1 BULK FERROFLUID. — If M_s is the saturation magnetization of bulk maghemite and v the volume of one particle, the magnetic susceptibility of an isotropic suspension of density N in particle is:

$$\chi_0 = \frac{1}{3} \mu_0 \frac{M_s^2 v^2}{kT} N$$

in the low field limit of the Langevin paramagnetism calculation. N is related to the particle volume fraction by: $N = \varphi/v$.

In the present case, we have in addition to take into account the particle diameter distribution, which follows a log-normal law:

$$P(D) \propto \frac{1}{D} \exp\left(-\frac{1}{2\sigma^2} \ln^2 \frac{D}{D_0}\right)$$

where $\ln D_0$ is the average value of $\ln D$ and σ is the standard deviation. We use the moment of

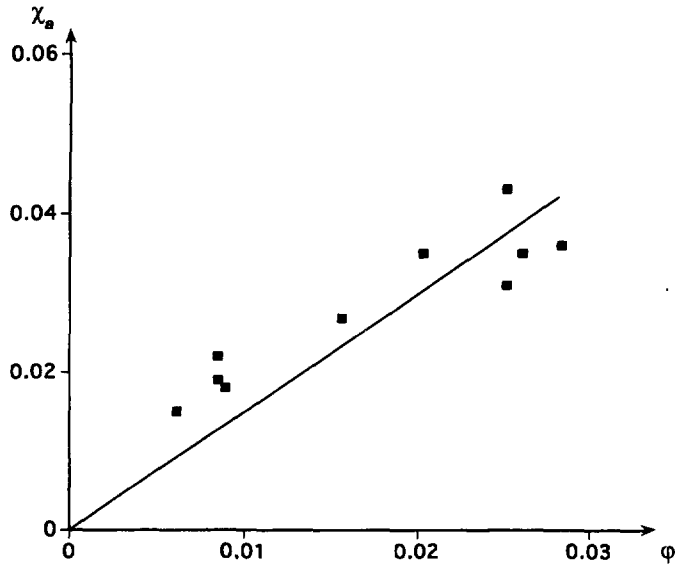


Fig. 5 — $\chi_a(\varphi)$ plot for the whole set of samples (SQUID measurements). The line corresponds to the affine function: $\chi_a = 1.5 \varphi$. Since χ_a is obtained by the difference between χ_{\perp} and χ_{\parallel} , the error bars are large: $\Delta\chi_a \approx \pm 0.01$.

order n of a log-normal distribution: $\langle D^n \rangle = D_0^n \exp\left(\frac{n^2}{2} \sigma^2\right)$ and then calculate the susceptibility, which is expressed as a function of the density N :

$$\chi_0 = \frac{1}{3} \mu_0 \frac{M_s^2}{kT} \left(\frac{\pi}{6}\right)^2 \langle D^6 \rangle N = \frac{1}{3} \mu_0 \frac{M_s^2 v_0^2}{kT} N \exp(18 \sigma^2), \quad (1)$$

where $v_0 = \frac{\pi}{6} D_0^3$

or as a function of the volume fraction φ :

$$\chi_0 = \frac{1}{3} \mu_0 \frac{M_s^2}{kT} \frac{\pi}{6} \frac{\langle D^6 \rangle}{\langle D^3 \rangle} \varphi = \frac{1}{3} \mu_0 \frac{M_s^2 v_0}{kT} \varphi \exp(13.5 \sigma^2).$$

Taking for D_0 and σ the values determined by small-angle scattering experiments: $D_0 = 58 \text{ \AA}$ and $\sigma = 0.4$, we find $\alpha_0 = 13.4$, which is in good agreement with the experimental value $\alpha_0 \approx 13.3$.

4.2 ANISOTROPY OF THE FERROSMECTIC PHASES. — The present experiments confirm the existence and sign of the magnetic anisotropy of ferrosmectic phases, which accounts for the instabilities observed in a magnetic field [6]. Besides, they show that the anisotropy depends in a linear way on the particle volume fraction. Although it may seem intuitive that magnetic anisotropy exists in a layered medium, the microscopic interpretation of this effect is in fact delicate enough to be discussed in detail: the nature of the coupling occurring between the smectic structure and the particles can *a priori* be of several types, and it is necessary to analyze the different possible mechanisms to identify the actual predominant one.

4.2.1 Dipolar field. — The dipolar field created by a magnetic particle is anisotropic. We first consider the consequences of this anisotropy in the case of an assembly of magnetic particles distributed in layers : each particle is submitted to an external field, plus the dipolar field created by its neighbors, which is different whether the external field is parallel or perpendicular to the layer : this is the equivalent of a demagnetizing field effect in two dimensions [9, 10]. Only the neighbors in the same layer are considered in a first step.

Following Widom [9], we consider the lamellae as monolayers of particles : the number of particles by unit surface is n_s and each particle bears a moment \mathbf{m} . We note b the total diameter of the particles, including the surfactant layer : b corresponds to the distance at contact and is equal to 9 nm [3]. The dipolar field \mathbf{h} is :

$$\mathbf{h} = \int \frac{d\mathbf{m}}{4\pi r^3} \left(3 \left(\frac{\mathbf{m} \cdot \mathbf{r}}{r} \right) \frac{\mathbf{r}}{r} - \frac{\mathbf{m}}{r} \right) = \frac{n_s}{4b} \mathbf{m}.$$

when the external field is parallel to the lamellae

and

$$\mathbf{h} = -\frac{n_s}{2b} \mathbf{m}.$$

when the external field is perpendicular to the lamellae.

The magnetization is $M_i = \frac{n_s m}{d} = \chi_0 (H_{\text{ext}} + h) = \chi_i H_{\text{ext}}$ with $i = \parallel$ or \perp , and thus we find to the second order in φ :

$$\begin{aligned} \chi_{\parallel} &= \frac{\alpha_0 \varphi}{1 - \alpha_0 \varphi d/4b} \sim \alpha_0 \varphi + \frac{d}{4b} \alpha_0^2 \varphi^2 \\ \chi_{\perp} &= \frac{\alpha_0 \varphi}{1 + \alpha_0 \varphi d/2b} \sim \alpha_0 \varphi - \frac{d}{2b} \alpha_0^2 \varphi^2 \\ |\chi_a| &\sim \frac{3d}{4b} \alpha_0^2 \varphi^2 \end{aligned}$$

In this expression, the dependence of χ_a on φ is quadratic. This quadratic variation is also obtained in a bulk demagnetisation field calculation, and is due to the fact that the mean dipolar (or demagnetising) field in the sample is proportional to the density of moments. Moreover, even a more sophisticated model taking into account the particle correlations, such as the one developed by Widom and Zhang [10], gives the same quadratic dependence, which appears thus as intrinsic to the dipolar field model. On the contrary, the numerical prefactor is strongly dependent on the approximations of the model, and is in particular decreased when considering the effect of neighboring layers in the above calculation : a numerical estimation leads to a decrease of the relative anisotropy $|\chi_a|/\chi_{\parallel}$ of a 2 %-ferrosmectic phase from 55 to 2 % when taking 2 000 adjacent layers into account.

Coming now to the comparison with our experimental values, we see that this calculation does not agree with the linear law observed. We conclude that the dipolar field effect, which certainly exists in the system, is not dominant in the range of volume fraction investigated here, and that the experimental accuracy does not allow us to measure it.

Since a model simply relying on an anisotropic repartition of magnetic dipoles is inadequate to describe the interactions occurring in our system at a microscopic scale, we consider, in a further step, the even more anisotropic case of particles with a shape anisotropy.

4.2.2 Anisotropic particles. — In a ferrofluid, there are *a priori* several mechanisms that may account for the existence of anisotropic objects, such as for instance the magnetic attraction between particles resulting in the formation of temporary pairs. This point will be carefully discussed later. In a first step, we will calculate the effect of anisotropic objects on the susceptibilities of the system.

We assume that a fraction of the particles, whose number per unit volume is N_2 , is associated in pairs, whereas N_1 is the density of single particles. This description with two different populations leads [10] to a ferrofluid susceptibility which is different from expression (1) :

$$\chi_0 = \frac{1}{3} \gamma \mu_0 \frac{M_s^2 v_0^2}{kT} N_1 + \frac{2}{3} \gamma \mu_0 \frac{M_s^2 v_0^2}{kT} N_2, \quad \text{where } \gamma = \exp(18 \sigma^2). \quad (2)$$

In the ferromagnetic phases, we assume that the existence of layers modifies in an anisotropic way the superparamagnetic properties of those few chained particles : we assume that the paired particles are prevented from freely rotating because of the confining membranes around them. In the parallel (resp. perpendicular) configuration, the orientational Boltzman distribution of particle moments considered in the Langevin calculation has to be truncated at a value θ_0 which is the maximum (resp. minimum) angle allowed between the moments and the external field. This angle θ_0 is related to the size of the paired particles and the periodicity of the lamellar structure (cf. Fig. 6). In this case, the ferromagnetic susceptibilities are :

$$\begin{aligned} \chi_{\parallel} &= \frac{1}{3} \gamma \mu_0 \frac{M_s^2 v_0^2}{kT} N_1 + \gamma \left(1 - \frac{1}{3} p^2\right) \mu_0 \frac{M_s^2 v_0^2}{kT} N_2 \\ \chi_{\perp} &= \frac{1}{3} \gamma \mu_0 \frac{M_s^2 v_0^2}{kT} N_1 + \frac{2}{3} \gamma p^2 \mu_0 \frac{M_s^2 v_0^2}{kT} N_2 \end{aligned}$$

with $p = \cos \theta_0$.

The anisotropy is finally given by : $\chi_a = (p^2 - 1) \gamma \mu_0 \frac{M_s^2 v_0^2}{kT} N_2$

and thus

$$\frac{|\chi_a|}{\chi_{\parallel}} = \frac{3(1 - p^2) N_2}{N_1 + (3 - p^2) N_2}$$

In order to determine the anisotropy χ_a , the two densities N_1 and N_2 have now to be evaluated. Two different mechanisms for pair formation are successively considered.

The first one directly ensues from the thermodynamic equilibrium of a colloidal suspension. The stability of a ferrofluid is achieved by preventing aggregation due to attractive inter-particles interactions. On the one hand, the van der Waals attraction, which is significant at very short distances only, is non-effective because the particles are protected by a surfactant coating. On the other hand, the long-range magnetic dipolar attraction is balanced by thermal agitation, and leads to a thermodynamic equilibrium between isolated particles and a small population of chained aggregates. This equilibrium is characterized by a coupling parameter λ , which compares the magnetic and thermal energy [7, 11] : $\lambda = \frac{E_d}{2 kT}$, where E_d is the energy of dipolar interaction between two particles at contact. For a monodisperse suspension of particles of magnetic volume $v = \frac{\pi}{6} D^3$ and total volume $v_t = \frac{\pi}{6} b^3$ including the surfactant layer, this coefficient is :

$$\lambda = \mu_0 \frac{M_s^2 v}{24 kT} \frac{D^3}{b^3}.$$

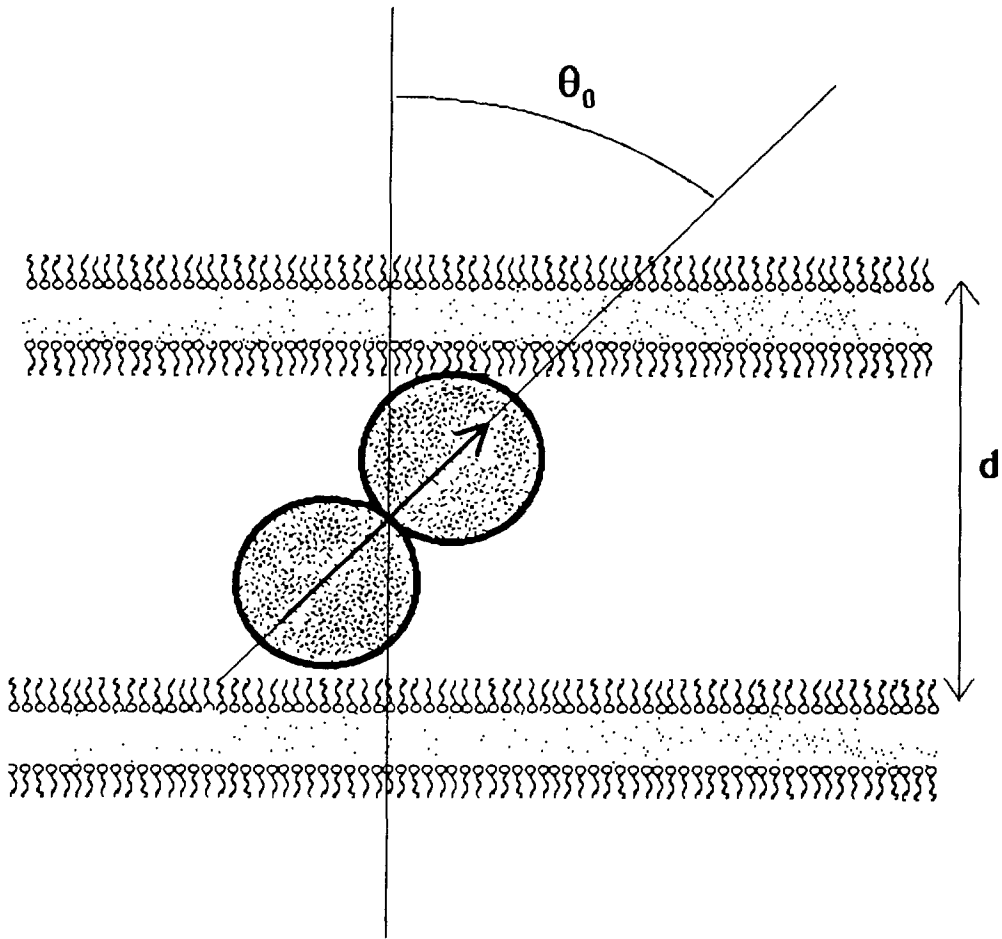


Fig. 6. — Sketch of a pair of particles prevented from freely rotating by the presence of hindering membranes.

and for a real ferrofluid with a log-normal size distribution :

$$\lambda = \mu_0 \exp(13.5 \sigma^2) \frac{M_s^2 v_0 D_0^3}{24 kT h_0^3}$$

We have determined experimentally the parameters involved in this expression for the ferrofluid used in this study and we can calculate : $\lambda = 0.5$, which means that we are in the case of a weak coupling between particles. The magnetic interactions between particles are small enough to be overcome by thermal agitation, and there is in fact no temporary thermodynamical pairing.

We should now consider permanent anisotropic objects, to which the same mechanism of hindered rotation due to the lamellar confining is applied, and whose existence may result from the synthesis of the ferrofluid. It must be emphasized that the methods we use to characterize the ferrofluid do not show any evidence of the existence of such anisotropic objects, so that their number, if any, is very small. These anisotropic particles will be described as permanent

pairs. Their relative amount does not vary when the ferrofluid is diluted, so that the density of paired particles N_2 is proportional to φ . The relation between the density of paired particles and the total particle density is written $N_2 = \epsilon N$, with $\epsilon \ll 1$.

The anisotropy of magnetic susceptibility of the ferrosmectic phases becomes :

$$\chi_a = \gamma(p^2 - 1) \mu_0 \frac{M_s^2 v_0^2}{kT} \epsilon N$$

and is now proportional to the volume fraction in particles φ .

With the estimate $p^2 \sim 0.5$, one can calculate the amount of pairs corresponding to the value $\frac{|\chi_a|}{\chi_{\parallel}} = 0.13$. We obtain $\epsilon \approx 0.10$; and we can thus successfully account for the ferrosmectic

anisotropy by the existence and confining of only five percent of pairs (i.e. ten percent of paired particles). By the small-angle scattering technique that we use for the characterization of the ferrofluid [2], it is not possible to discriminate between form and size polydispersity, so that a small amount of anisotropic pair-like particles can be hidden by the large-size part of the log-normal distribution of particle diameters. Nevertheless, the existence of field induced birefringence in similar ferrofluids [12] can be considered as an indication of the presence of anisotropic objects.

It is interesting to point out that the argument of restricted rotation also accounts for the observed variation of χ_a with the lamellar periodicity d : when the periodicity increases, so does the available space between membranes and χ_a is expected to decrease. These predictions are in qualitative agreement with our results. In fact, the model predicts the existence of a cross-over towards a non-hindered rotation regime when d is large enough, but the approximations that have been made in the calculation — shape of the anisotropic particles approximated by the shape of a pair and out-of-plane fluctuations of the membranes neglected — make a quantitative analysis of this cross-over delicate.

Finally, a model based on the existence of a small amount of permanent pairs in the system accurately describes the behavior of the magnetic susceptibility of a ferrosmectic phase. The other mechanisms that have been considered should nevertheless contribute to the anisotropy of the susceptibility and one can expect to confirm their relevance by performing experiments for larger particle volume fractions, where χ_a should be quadratic with φ .

Conclusion.

Ferrosmelectics, which are lamellar phases with magnetic particles inserted between their layers, actually achieve bidimensional magnetic fluids. As such, they possess an anisotropy of magnetic susceptibility, whose experimental study is reported here. Both the parallel and perpendicular susceptibilities of these phases are high, as expected from a superparamagnetic system, and their difference is large, of the order of 13 %, showing that the system is indeed strongly anisotropic.

Surprisingly enough, the variation of the anisotropy of susceptibility with the fraction of particles cannot be interpreted in the framework of mean-field-type processes, involving the anisotropy of the dipolar magnetic field or magnetic coupling of particles. On the contrary, the experimental results are successfully explained by the existence of a very small population of permanently paired particles in the suspension, whose rotation is hindered by the lamellar structure.

In conclusion, ferrosmectic phases present very specific features, by comparison to analogous systems such as thermotropic smectics, whose diamagnetic susceptibilities and relative anisotropy are several orders of magnitude smaller. Additional work is currently under

way to study the even more anisotropic objects obtained by inserting magnetic particles in the cylinders of a lyotropic hexagonal phase [13].

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References

- [1] Fabre P., Casagrande C., Veysse M., Cabuil V. and Massart R., *Phys Rev Lett* **64** (1990) 539.
- [2] Fabre P., Ober R., Veysse M. and Cabuil V., *J Mag Mag Mat* **85** (1990) 77
- [3] Ponsinet V., Fabre P., Veysse M. and Auvray L., *J Phys II France* **3** (1993) 1021
- [4] Fabre P., Quiliet C., Veysse M., Nallet E., Roux D., Cabuil V. and Massart R., *Ltrophys Lett* **20** (1992) 229
- [5] Fabre P. *Mat Res Soc Symp Proc* **248** (1992) 55
- [6] Ponsinet V., Fabre P. and Veysse M., to be published
- [7] Rosensweig R. E. *Ferrohydrodynamics* (Cambridge University Press, Cambridge, 1985)
- [8] Shliomis M. I., *Sov Phys Usp* **17** (1974) 153.
- [9] Widom M., private communication
- [10] Widom M. and Zhang H., *Mat Res Soc Symp Proc* **248** (1992) 235
- [11] de Gennes P. G. and Pincus P. A., *Phys kondens Materie* **11** (1970) 189
- [12] Bacri J.-C., Dumas J., Gorse D., Perzynski R. and Salm D., *J Phys Lett* **46** (1985) L-1199
- [13] Quiliet C., Ponsinet V. and Cabuil V., *J Phys Chem* **98** (1994) 3566