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Short Communication

Modification of the Interactions in a Lamellar Phase by the Presence of Nanoparticles

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Abstract. — A ferrosmectic is a swollen lamellar phase in which solid magnetic particles have been incorporated. We measure the elastic constants of these phases, and compare them to conventional lyotropic smectic phases. It is shown that both the bending and the compression elastic constants are largely enhanced by the presence of particles and that their evolution can not be accounted for by the usual models for lamellar phases. A phenomenological model of enhanced repulsive potential between membranes based on steric considerations is developed and confronted to experimental results.

Introduction

Recently, a new class of hybrid lyotropic systems has been invented and studied: they are constituted of a complex fluid doped with solid nanoparticles [1, 2]. A singularly interesting system is the magnetic smectic phase, called ferrosmectic, where magnetic oxide particles of size 10 nm are included in the oil layers of a swollen lamellar phase [3]. The resulting system is a stack of quasi-bidimensional magnetic layers separated by thin membranes. One of the studies undertaken on this system, by a neutron scattering technique [3], has displayed striking differences compared to conventional lamellar phases. Since the features of small-angle neutron scattering spectra are related to the elasticity of the system, it is clear that the addition of particles does modify it. In this paper, we present the experimental determination of the elastic constants and of the quantitative influence of the particles; we propose a model to understand their behavior.

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Experimental Results

The system studied has been described in detail in reference [3]. The ferrosmectic phase is obtained by swelling a pentanol/SDS(sodium dodecyl sulfate)/water mixture with a magnetic liquid, called a ferrofluid, which is a dispersion of maghemite ferrimagnetic 6 nm-diameter particles [4] in cyclohexane. The relevant parameters are the smectic periodicity d , which can vary from 20 nm to 45 nm, and the volume fraction of particles ϕ , which was varied in the range 0.3% to 4%. The evolution of the membrane flexibility κ with the content of co-surfactant and particles has been determined in conventional and doped systems *via* small-angle scattering experiments along dilution lines [5, 6]: κ strongly depends on the alcohol content, but not on the concentration of the particles. The samples studied here were located on dilution lines of minimal content in alcohol, which minimum content depends on the particle volume fraction [1]. As a result, the membrane flexibility κ is not the same in all the samples: the corresponding evolution of κ/d with ϕ is presented in Figure 2.

The elasticity of a lamellar phase is described by two constants: K is the bending elastic modulus and \bar{B} is the compression modulus at constant chemical potential. The free energy density is then, with $u(x, y, z)$ the displacement of the membrane [7]:

$$F_{\text{el}} = \frac{1}{2}K \left(\frac{\partial^2 u}{\partial x^2} + \frac{\partial^2 u}{\partial y^2} \right)^2 + \frac{1}{2}\bar{B} \left(\frac{\partial u}{\partial z} \right)^2$$

Two different experiments were performed, that measure different combinations of K and \bar{B} , and their variation with the concentration in magnetic particles. One of those combinations is the smectic penetration length λ , which is equal to $\sqrt{K/\bar{B}}$; it was determined *via* the analysis of the defect pattern induced in a cell with a thickness gradient [8]. Another experiment allows us to determine the product $K\bar{B}$: in a magnetic field, above a threshold value, the smectic layers of the ferrosmectic reorient. This reorientation occurs at low field through the appearance of localized defects [9]. It is worthwhile noting that this method leading from the measurement of a threshold field of reorientation to informations about the elasticity of a liquid crystal has been classically used in nematic or cholesteric phases; it can be applied to this particular smectic because it exhibits not only a large magnetic susceptibility, but also a very high anisotropy of this susceptibility [10]. We have elaborated a model that interprets the experimental results and provides an expression for the threshold field, related to the elastic constants [9]:

$$H_C = C \sqrt{\frac{4}{\mu_0 \chi_a h}} (K\bar{B})^{1/4}$$

where χ_a , the anisotropy of the magnetic susceptibility, was previously shown [10] to increase linearly with ϕ , h is the sample thickness and C is a numerical prefactor of order one.

The threshold field was measured, as described in reference [9], as a function of the particle volume fraction, with samples of constant swelling ratio such that $d = 30$ nm. We then extract $C^4 K\bar{B}(\phi)$.

In order to obtain the prefactor C , the experimental values of $C^4 K\bar{B}$ extrapolated for $\phi = 0$ are adjusted to the value of $K_0 \bar{B}_0$ for equivalent nondoped systems. We find $C \approx \sqrt{2}$, and determine the variation of $K\bar{B}$ with ϕ displayed in Figure 1.

From these measurements and the previous determination of λ [8], we obtain the first quantitative determinations of K and of \bar{B} for ferrosmectic systems; their evolutions with the volume fraction ϕ at constant swelling ratio are plotted in Figures 2 and 3. Notice first that both K and \bar{B} are considerably enhanced compared to their values in the initial non-doped

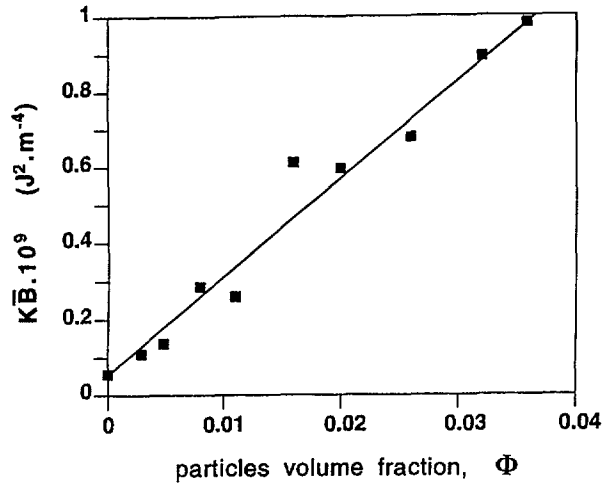


Fig. 1. — Evolution of the product $K\bar{B}$ with the particles volume fraction ϕ , deduced from the measurement of the threshold magnetic field. The line is a guide for the eyes.

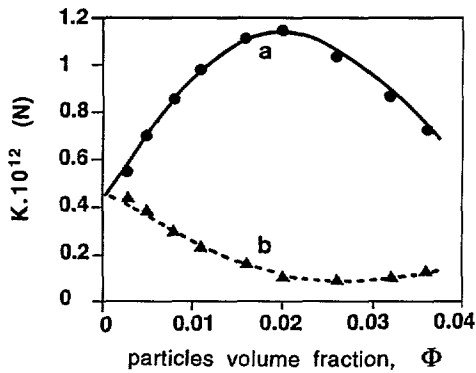


Fig. 2.

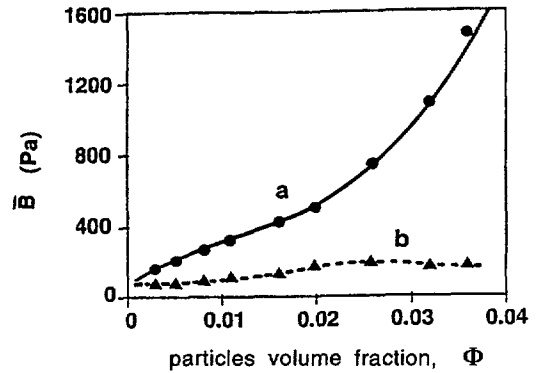


Fig. 3.

Fig. 2. — Evolution of the bending modulus K with the volume fraction ϕ : a) experimental data; b) calculated values from the relationship $K = \kappa/d$.

Fig. 3. — Evolution of the compression modulus \bar{B} with the volume fraction ϕ : a) experimental data; b) calculated values from the Helfrich model.

phase: a ferrosmectic phase is both less flexible and less compressible than a conventional lamellar one. The behaviors of K and \bar{B} are nevertheless different: \bar{B} is constantly increasing with the concentration of particles, up to an order of magnitude above $\phi = 0$ for $\phi = 4\%$, while K exhibits a non-monotonic variation.

In the following, we will interpret the specific compressibility of ferrosmelectics by modified intermembrane interactions, we will discuss the specific bending constant, and check the consistency of our measurements and considerations.

Interpretation

Let us recall that in a classical lyotropic smectic with screened or no electrostatic interactions, the stabilizing interaction potential is derived from the steric hindrance of the thermal fluctuations of the membranes, as described by Helfrich [11]. The corresponding interaction potential reads: $V(d) = \frac{3\pi^2}{128} \frac{(kT)^2}{\kappa(d-\delta)^2}$. In this case, both elastic constants K and \bar{B} are related to the membrane flexibility κ and the periodicity d of the system through [11,12]:

$$K = \kappa/d \quad (1)$$

and

$$\bar{B} = d \left[\frac{d^2 V(\ell)}{d\ell^2} \right]_{\ell=d} = \frac{9\pi^2}{64} \frac{(kT)^2}{\kappa} \frac{d}{(d-\delta)^4} \quad (2)$$

where δ is the membrane thickness. Since κ , K , and \bar{B} have been measured independently, the validity of these relationships can be tested in a ferrosmectic medium. Figures 2 and 3 present, in addition to the values measured for K and \bar{B} , the values calculated from (1) and (2), using the previous determination of κ : there is obviously a strong discrepancy between the predicted and experimental results. This shows, quantitatively for the first time, that the Helfrich potential is not adequate to describe the interactions in a ferrosmectic system.

In order to interpret the measured values of \bar{B} , we have elaborated a specific model of the interaction potential between membranes. We assume that the presence of particles induces a steric hindrance of the membrane fluctuations and thus a reduction of their amplitude. This effect is taken into account by considering that, if d is the periodicity of the phase, the amplitude of the membrane fluctuations is the same as would occur in a phase without particles but of periodicity $d - L$. The phenomenological length L thus represents the excluded region for the membranes, which *a priori* should depend on the particle concentration (*cf.* Fig. 4 Insert). Using $d - L - \delta$ instead of $d - \delta$ as the characteristic distance available for the position fluctuations of each membrane whereas d remains the equilibrium periodicity of the smectic, it is thus possible to derive a new relationship between κ and \bar{B} :

$$\bar{B} = \frac{9\pi^2}{64} \frac{(kT)^2}{\kappa} \frac{d}{[(d-L)-\delta]^4} \quad (3)$$

Fitting the experimental curves with this expression, one obtains the dependence of the length L with the volume fraction of particles, as shown in Figure 4a, where the quantity $(L + \delta)$ is plotted *versus* ϕ . Notice that $(L + \delta)$ is increasing with ϕ , and always lies between δ , the membrane thickness, and $d/2$, where d is the periodicity of the smectic: these values of L are physically reasonable and support the validity of our description.

Turning now to the bending constant K , the discrepancy between K and κ/d remains to be understood: in classical systems, the relation (1) expresses the bulk modulus of a smectic as a superposition of the elasticity of each membrane, with a density $1/d$. The experimental results presented here show that this relation is not valid in the case of ferrosmectic phases. Since the relation (1) is widely considered to be independent of intermembrane interactions, we make the hypothesis that the discrepancy is due to an additional rigidity given to the system by layers of particles of same density $1/d$: $K = \kappa/d + g(\phi)/d$. This description still requires a microscopic interpretation to understand in particular how the contribution of the particles depends on their concentration.

The experimental values of the elastic constants K and \bar{B} determined above can be confronted to the features of the neutron scattering spectra. The comparison with small angle

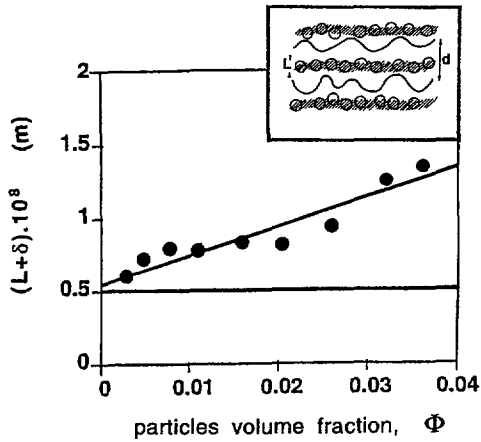


Fig. 4.

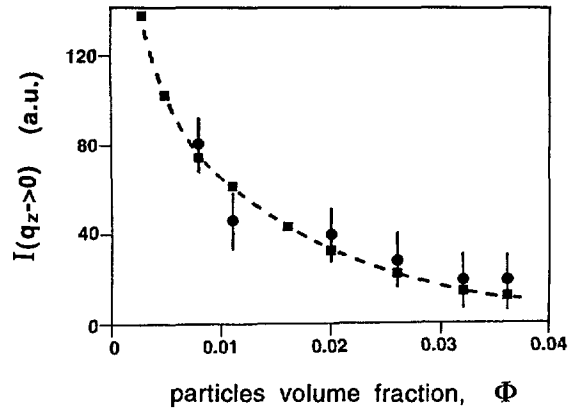


Fig. 5.

Fig. 4. — Variation of the length $L + \delta$ with ϕ deduced from the model of steric hindrance and the experimental data. The line is a guide for the eyes. Insert: Schematic representation of the excluded region L due to the steric hindrance of the particles.

Fig. 5. — Evolution of the intensity scattered at small-angle as a function of volume fraction: (●) experimental data; (■) calculated according to (4b).

scattering experimental results also constitutes a validation of our hypotheses of modified intermembrane interactions. Indeed, let us recall that the ferrosmectic scattering spectra drastically differ from lamellar phases in several points [3]: non-monotonic variation of the Bragg peak intensity, appearance of a second order, strong decrease of the small angle scattering. As for the two first characteristics, the scattered intensity only depends on the constants K and \bar{B} and the smectic periodicity, and can thus be recalculated from the experimental values obtained above. The agreement is indeed very satisfactory [5].

As for the intensity at very low angles, it has been shown to be [13]:

$$I(q_z \rightarrow 0) \propto kT\chi \frac{B}{\bar{B}} \quad (4)$$

where χ is the osmotic compressibility of the membrane and B the compression elastic modulus at constant membrane concentration. Taking into account the expressions of the elastic constants and the expressions for χ and B as functions of κ , d , and δ in the case of conventional entropic phases, the intensity $I(q_z \rightarrow 0)$ can be calculated:

$$I(q_z \rightarrow 0) \propto \delta^2 \kappa d \left[\frac{d - \delta}{d} \right]^4 \quad (4a)$$

For ferrosmelectics, the calculation of the small-angle scattered intensity within the physical hypotheses of the model gives:

$$I(q_z \rightarrow 0) \propto \delta^2 \kappa d \left[\frac{d - L(\phi) - \delta}{d} \right]^4 \quad (4b)$$

If we then calculate this intensity with the values previously and independently determined for δ , d , κ , and L , we find that $I(q_z \rightarrow 0)$ does strongly decrease when the particles volume fraction

is increased. The order of magnitude of this decrease is in agreement with our experimental observations, as shown in Figure 5.

In summary, we have proven the consistency between independent experimental determinations of the elastic constants of ferrosmeectics, the phenomenological model presented above and the features of neutron scattering spectra.

Conclusion

Ferrosmeectics, which are hybrid lamellar phases, are expected to display new and original features. In this paper, we have shown that the presence of host solid particles not only allows access, through their magnetic response, to some of the very fundamental properties of lamellar phases, such as their elasticity, but also is responsible for drastic differences in the properties of the systems compared to their nondoped analogues. Using two different experimental methods, we have determined the elastic constants of ferrosmeectics *versus* the amount of particles incorporated between their layers. The very unusual behavior of these constants has led to the conclusion that the well-known Helfrich potential alone cannot be responsible for the stability of the phases, and that another type of interaction mediated by the particles had to come into play. A phenomenological model based on the idea of steric hindrance of the particles has been able to account for our experimental results, unifying such different experimental data as those coming from neutron scattering and from typical liquid crystalline methods.

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