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Surface-induced ordering in ionic and surfacted magnetic fluids

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The wetting of a glass surface by ionic and surfacted ferrofluids is discussed. Optical experiments are used to investigate the existence of an ordering in a thin ferrofluid layer stabilized by the glass surfaces. The experimental results indicate that the ferrofluid wetting on a glass surface having an optical axis orients the magnetic grains perpendicularly to the glass optical axis. [S1063-651X(97)50308-4]

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It is well known in the physics of liquid crystals [1] that a solid or gas interface can organize the molecules of these complex anisotropic fluids into a structure different from that present in the bulk. This surface stabilizing effect can be interpreted as a surface field that couples the molecules of the liquid crystal in the vicinity of the interface and induces this ordering. The interaction between the surface and the molecules is usually due to van der Waals forces, but adsorption mechanisms may also be present.

In the case of lyotropic nematic liquid crystals [2], which are mixtures of amphiphilic molecules and a solvent, the solid substrate in contact with the fluid stabilizes a lamellar layer [3] that prevents the direct interaction between the micelles and the solid surface. The lamellar layer stabilized has essentially a smecticlike structure [4] and, in the bulk, the symmetry remains nematic.

On the other hand, to our knowledge, this kind of symmetry breaking has not been observed in a complex isotropic fluid such as a ferrofluid [5]. These materials are colloidal suspensions of magnetic grains dispersed in a liquid carrier. The typical dimension of the grains is 100 Å. Under usual conditions these fluids are isotropic like any isotropic liquid and have a high magnetic susceptibility. These properties lead to numerous industrial applications such as rotating seals, loudspeakers, and so on [5,6].

Two different types of ferrofluids are available: surfacted ferrofluids (SFF) and ionic ferrofluids (IFF). SFF are usually nonaqueous and the classical manufacturing procedures are very long: nanoparticles of magnetic oxide are obtained by grinding and after that the grains are coated with surfactant agents to obtain a suspension in an organic solvent. These ferrofluids were extensively studied by means of optical and scattering techniques [7] and, in the absence of a magnetic field, the fluid remains isotropic. In 1980, a new mechanism of ferrofluid manufacturing was proposed [8]: colloidal magnetite grains are synthesized by alkaline condensation of Fe ions and, after being electrically charged, are dispersed in an aqueous solution.

Ferrofluids become optically anisotropic [9] when subjected to a magnetic field. This field-induced birefringence occurs in the bulk of the sample either by orientation of the magnetic grains or by secondary aggregation of large aggregates into strings. When the external field vanishes, these superstructures disappear and the fluid becomes isotropic again. Some puzzling results have been obtained with IFF by using optical and x-ray-scattering techniques without applying any magnetic field and by varying the sample temperature [10,11]. These results indicate the existence of a small optical birefringence (about 10^{-5}) in samples *without any external magnetic field*. In these experiments, the IFF sample was encapsulated in 0.2-mm-thick flat glass microslides and the optical anisotropy was considered essentially as a bulk property of the IFF.

In this paper, we study, by means of optical techniques, the effect of a flat glass surface in contact with the grains of ferrofluids of both types, SFF and IFF.

The SFF used has a commercial origin (Ferrofluidics). Grains are made of Fe_3O_4, with a typical diameter value of 100 Å. They are dispersed in water with two concentrations: $c_1 = 3.1 \times 10^{15}$ and $c_2 = 8.3 \times 10^{15}$ grains/cm^3. The IFF we studied has γ-Fe_2O_3 grains (nanoparticle colloids), with typical dimensions of 95 Å, dispersed in water with concentrations of $c_3 = 8.6 \times 10^{15}$ and $c_4 = 8.6 \times 10^{16}$ grains/cm^3. The sample is placed in a cylindrical fused quartz cell (Hellma, model. 121.000 QS), with the following geometrical characteristics: volume 210 μl; inner diameter 13 mm; inner height (sample thickness) 0.5 mm. Temperature is fixed at 25 °C. The cell is placed in a sample holder that enables the cell to rotate around its axis, (which coincides with the light-propagation direction). A complete rotation of the cell can be performed by 0.5° steps by means of a Newport rotating stage. The cell was washed with HCl and water before being filled with the ferrofluid.

The experimental setup consists of a CW 10-mW linearly polarized He-Ne laser beam ($\lambda = 6328$ Å) modulated by a photoelastic modulator ($w/2\pi = 50kHz$) which is sent through the sample along the rotation axis of the sample holder, followed by an analyzer. The x axis of the laboratory frame is horizontal and perpendicular to the light-propagation direction (z-axis). The setup is orientated in such a way that the earth's magnetic field ($\sim$0.5 G) was parallel to the x axis. Its eventual influence is discussed further. The polarizer direction is along the y axis. The angle between the analyzer and polarizer directions is 45°. One of the principal

axes of the modulator is parallel to the analyzer direction. The transmitted light is detected by a photodiode connected to a digital lock-in amplifier which gives the first time Fourier component of the transmitted signal (FTS) I_w . The experimental procedure consists in first measuring I_w with an empty cell, as a function of the angle θ between the x axis and an arbitrary x' axis fixed in the cell and, second, taking the same measurement with the cell filled with ferrofluid. This two-step procedure is adopted to reduce the number of parameters to be fitted simultaneously in the data analysis.

Figures 1(a)–1(c) give the measured FTS I_w curves as functions of θ for the empty glass cell and for the cells filled with IFF and with SFF, respectively. I_w curves obtained with ferrofluid samples exhibit clearly in Fig. 1, an angular shift with respect to that obtained with the empty cell. The angular shift is about 5° for both IFF and SFF. It is important to stress that this angular shift is determined by comparing the complete curves, not only their minimum positions. This fact proves the existence of a birefringent layer (or layers) due to the presence of the ferrofluid.

To analyze these results, let us consider the FTS given by a set of birefringent slabs in our experimental setup. The FTS of one birefringent slab positioned in the xy plane, is a function of the phase shift Ψ and the angle γ (taken positive when counterclockwise), between the optical axis of the slab and the x' axis. Simple matrix calculations give for I_w [12]

$$I_w = -E_0^2 J_1(a)\sin(\Psi)\cos\{2(\gamma+\theta)\}\sin(wt), \qquad (1)$$

where E_0 is the incident electric field $J_1(a)$ is the Bessel function of a defined by the phase shift δ of the photoelastic modulator [$\delta = a\ \sin(wt)$] and a is equal to $\pi/2$ in our device. Considering now the general case of a pile of birefringent slabs, the outgoing vector field E^o can be expressed as

$$E^o = \frac{E_0}{4}\begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} M_s \begin{pmatrix} 1-e^{i\delta} \\ 1+e^{i\delta} \end{pmatrix}, \qquad (2)$$

where the rightmost column vector represents the field at the output of the polarizer followed by the photoelastic modulator. M_s is the sequential product of Jones matrices, which characterizes the set of birefringent layers, and the leftmost matrix represents the Jones matrix of the 45° analyzer. In a general form, M_s can be written as

$$M_s = \begin{pmatrix} a_1 & a_2 \\ a_3 & a_4 \end{pmatrix}, \qquad (3)$$

the rotation angle θ being taken into account in the expressions of a_i ,which is not given here. Since I_w is the product of the outgoing field E^o by its complex conjugate, it can be written as

$$I_w(\ldots,\Psi_i,\gamma_i,\ldots) = E_0^2 J_1(a)\,\mathrm{Im}\{(a_1+a_3)(a_2+a_4)^*\}\sin(wt), \qquad (4)$$

where the angles Ψ_i and γ_i characterize the ith layer and where Im states the imaginary part of a complex variable. A Fourier analysis of Eq. (4) with regard to the function of θ shows that only three parameters can be determined from the study of a I_w curve for a rigid system (where γ_i do not depend on θ). Therefore, fitting more than three parameters in Eq. (4) would result in some indetermination in their values.

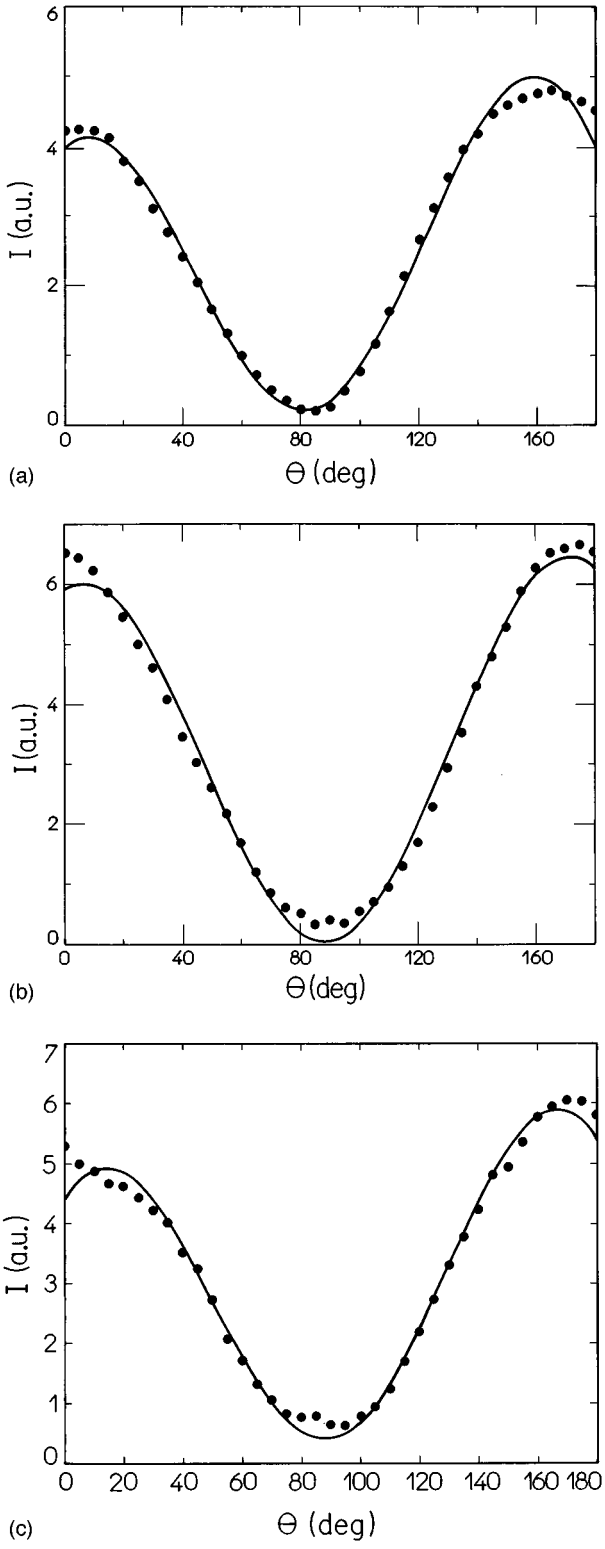

FIG. 1. Fundamental transmitted signal (FTS) I_w as a function of the angle θ. The solid lines are best-fit curves according to Eq. (4). (a) Empty fused quartz cell; (b) cell filled with ionic ferrofluid; (c) cell filled with surfacted ferrofluid.

We assume that our sample is a superposition of five layers: two birefringent glass layers from the cell, two birefrin-

TABLE I. Phase shift Ψ and orientation angles γ_1, γ_2 of two different layers.

	Ψ(deg)	γ_1(deg)	γ_2(deg)
quartz cell	0.222 ± 0.022	−82.8±1.7	−84.0±1.8
SFF (c_1)	0.102 ± 0.010	5.5±0.4	18.6±2.8
SFF (c_2)	0.157 ± 0.016	11.5±1.2	6.7±1.2
IFF (c_3)	0.110 ± 0.020	10.3±2.5	26.9±1.2
IFF (c_4)	0.152 ± 0.015	8.1±0.2	7.9±0.1

gent layers of ferrofluid film near the surfaces of the cell, and a bulk layer in between which is assumed to remain isotropic without any external magnetic field. The total number of parameters to be determined exceeds three; this is the reason their evaluations are made in two steps.

The first step of our analysis consists in fitting parameters of Eq. (4) to experimental FTS I_w data versus θ for the empty cell, considering that it is a superposition of only two layers with the same values for Ψ but with different orientations γ. The assumption that the two glass substrates have the same value of Ψ enables one to reduce to three the number of parameters to be fitted but is also justified by the fact that both flat surfaces of the cell were made with the same fused quartz (technical information provided by the Hellma Co.). The results Ψ, γ_1, and γ_2 are given in Table I (error estimations are discussed further) and the corresponding plot is shown in Fig. 1(a).

The second step of the determination is the fitting of Eq. (4) to the experimental data obtained with the cell filled with the ferrofluid, considering the superposition of four successive birefringent layers. The first and the fourth layers are due to the cell, and their parameters are already known from the first step of the determination; the two layers in the middle are due to ferrofluid. As for the empty cell walls, the values of Ψ are assumed to be equal in both ferrofluid layers. The best-fit values found for Ψ, γ_1, and γ_2 are given in Table I and plotted in Figs. 1(b) and 1(c).

The birefringence observed in the glass cell is probably due to residual stresses, stria, or even inclusions in the fused quartz substrates whose characteristics may change from one place to another. As in our model, Ψ is assumed to be a constant value versus θ; the impact point of the laser beam on the cell must not vary as the sample is rotated. This point is the main source of uncertainties in this measurement and much care must be taken about it.

Uncertainties given in Table I are obtained in two steps using the following procedure. In the first step, for each sample, empty glass cell or cell filled with ferrofluid, five independent measurements are performed and the values for Ψ, γ_1, γ_2 are determined. The sample holder is cleaned as described above and filled with ferrofluid and then another determination of Ψ, γ_1, γ_2 is performed. The uncertainties are evaluated by taking into account *the maximum deviation in the values of the fitting parameters*. They are not simply associated with the computer fitting procedure. These uncertainties in Ψ are about 0.5%, 3%, 7%, 18%, and 1% in the case of the glass substrate, samples c_1, c_2, c_3, and c_4, respectively. In the second step, we evaluate the uncertainty introduced by the hypothesis of the same Ψ for the two glass substrate walls. To do that, we measured Ψ of the glass substrates (following our previous procedure, i.e., the same value of Ψ in both walls), varying several times the impact point of the incident laser beam in the empty sample holder. The maximum variation of Ψ obtained was about 10%. At this point we assume that *this is the maximum difference between the two Ψ values of both walls of the glass sample holder*. Now we introduce these two 10% different values of Ψ to fit the ferrofluid surface layer parameters and evaluate their uncertainties. The maximum deviation in the values of Ψ of the ferrofluid layers obtained with this procedure was about 8%. The uncertainties presented in Table I are the largest obtained in both steps. We assumed an uncertainty of 10% in the values of Ψ of all the samples, with the exception of c_3, where the uncertainty obtained in the first step evaluation is about 18%.

The values found for γ with ferrofluid samples indicate that this effect cannot be connected *trivially* to the earth's magnetic field, which points along the x axis. The birefringence induced by the earth's magnetic field in the bulk of the sample was estimated [13] and was shown to introduce a phase shift $\ll 0.02°$. The role of the bulk layer in the middle of the sample can be neglected in our analysis, which reduces our study to that of a four-layer rigid system only. If the bulk birefringence induced by the earth's magnetic field could not be neglected, the system to be studied according to Eq. (4) would not be a rigid one any more. To verify this point, an independent experiment is made with a cell filled with ferrofluid, where the optical axis of the glass cell is oriented at an angle of about $-106°$ with respect to the x' axis. The fitting procedure is the same as before and we obtained, typically, for the IFF (c_4), $\Psi = 0.151°$, $\gamma_1 = -8.2°$ and $\gamma_2 = -6.7°$. Comparing these values with those of the last row of Table I, we conclude that the value of Ψ is the same, within our accuracy range, as the one obtained in the previous experiment. As expected, it is independent of the relative orientation of the glass cell with respect to the x' axis; the values of γ_1 and γ_2 are now negative and differ about 16° from those given in Table I (around $+8°$). This result indicates that the direction of the optical axes of the ferrofluid layers is connected to the direction of the glass cell optical axis.

To check our experimental observations, the same experiment is performed with two different isotropic fluids, water and ethanol. The values obtained for Ψ, γ_1, and γ_2 coincide, within our experimental accuracy, with those found with the empty cell. As in the case of anisotropic fluids, a glass bounding surface seems to stabilize a ferrofluid birefringent layer on it. This anisotropic wetting by the ferrofluid, which breaks the C_∞ symmetry around the normal to the glass surface, can be due to van der Waals interactions among the grains and the surface, and is probably dependent on the easy axis [4] of the surface. The value of Ψ obtained with the two different types of ferrofluids indicates that their ionic or surfacted character is not relevant for this parameter. On the other hand, Ψ is an increasing function of the concentration of the sample. The influence of concentration on Ψ seems to be less important in IFF than in SFF in which a $3\times$ increase in the concentration gives the same effect as a $10\times$ increase in the IFF concentration.

The values of γ_1 and γ_2 of the quartz cell (first row of Table I) indicate that the optical axes of the glass walls are

almost parallel (around $-84°$). All the values of γ_1 and γ_2 obtained for both ferrofluids are in the range of about 5°–26°, which corresponds to a direction almost perpendicular to the cell glass optical axis. This effect was also clearly verified when the optical axis of the glass cell was rotated by about $-106°$, and $\gamma_1=-8.2°$ and $\gamma_2=-6.7°$ (c_4 sample). This result indicates that the wetting process of the ferrofluid on the glass surfaces tends to orient the grains perpendicularly to the glass optical axis. The interpretation of this result is not straightforward. It seems to indicate that in some way the optical axis of the glass cell wall is connected not only to the bulk properties of the glass, but *also to the nature of the glass surfaces*. As discussed before, glass surfaces that exhibit channels and undulations may orient the liquid crystals put in contact with them. We can suggest a possible mechanism that could be responsible for the orientation of the magnetic grains in contact with the surface: if the surface has microscopic channels, formed during the manufacturing process, oriented along the optical axis, these channels could orient, by means of a mechanical coupling, the anisotropic ferrofluid grains.

Let us discuss now the possible relation between the results of this paper and the previous observation [10,11] of a small birefringence (10^{-5}) in IFF placed in glass microslides, without any applied magnetic field. These sample holders present [3,14] a large number of channels (and stria) along their long axis. These channels probably favor the orientation of the ferrofluid grains on the glass surfaces during the wetting. Accordingly, a ferrofluid layer is expected to be present on each inner glass surface of the microslides. In thin samples (in Refs. [10,11] the maximum sample thickness was 200 μm), the surface layers could even influence the orientation of the ferrofluid grains in the bulk. This residual bulk birefringence could be present in the one reported in [10,11].

In conclusion, the wetting of a glass surface (which has an optical axis) by ferrofluids induces the formation of a layer on it, where the magnetic grains are oriented. To investigate the origin of this anisotropic wetting and its relation to the properties of the surface and the magnetic fluid, new optical and x-ray scattering experiments need to be performed.

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