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Nature of ferronematic alignment in a magnetic field

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Ferronematics are stable liquid crystal dispersions with high magnetic susceptibility. Although predicted many years ago (1970), they have been synthesized only recently. The experimental determination of the Fréedericksz transition critical field in ferronematics contradicts the earlier [Brochard and de Gennes, J. Phys. (Paris) **31**, 691 (1970)] assumption of strong anchoring between liquid crystal molecules and magnetic grains. Here an explanation consistent with the experimental results of the coupling between liquid crystalline and magnetic degrees of freedom is given. We explain that this coupling is due to steric interactions between anisometric liquid crystal micelles and ferroparticle clusters.

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The magnetic susceptibility of pure liquid crystals (LC's) is weak and a high external magnetic field ($H\sim1$ kOe) is usually needed to distort their texture [1]. In their pioneering work [2], Brochard and de Gennes proposed correcting this shortcoming of known LC's by introducing ferromagnetic particles inside a nematic LC matrix. Such hypothetical systems have been called *ferronematics*. Attempts to synthesize ferronematics have been undertaken for almost 30 years, but a stable dispersion of ferroparticles in a LC matrix was not achieved. In many cases [3,5] the lifetime of LC-ferroparticle dispersions did not noticeably exceed the measurement time. Previous authors [3–8] have studied liquid crystals doped with ferrofluids, that is, inhomogeneous dispersions of ferroparticles in LC matrices. These systems are not ferronematics in the Brochard–de Gennes sense, i.e., stable colloidal systems [1,2]. Only in a recent series of papers did Berejnov and co-authors [9–12] succeed in synthesizing stable ferronematics. They employed lyotropic LC and ferromagnetic maghemite (γ-Fe_2O_3) nanoparticles. These ferronematics remained stable even after storage for more than eight months. The authors achieved a volume fraction of magnetic particles of $\Phi=0.01$ and a magnetic susceptibility of $\chi=0.06$ (cgs units), which is four to six orders of magnitude higher than in pure LC's.

The question we address here is how an external magnetic field orients the LC matrix. Brochard and de Gennes [2] assumed that very long (~1000 Å), rodlike ferromagnetic grains in an external magnetic field modify the LC director due to specific coupling between ferroparticles and liquid crystal molecules. Since LC molecules are much smaller than magnetic grains, this coupling should be similar to the known surface anchoring between LC molecules and solid surfaces. Then they [2] developed a theory assuming strong surface anchoring between the LC matrix and magnetic grains. Later, in order to explain previous experiments [5], this model was generalized for the case of soft anchoring [13].

Stable ferronematics proved to be rather different from the Brochard–de Gennes picture. It has been established [9–12] that a lyotropic ferronematic solution is formed by discotic micelles of potassium laurate and 1-decanol molecules with a characteristic diameter ≈64 Å and thickness ≈23 Å, and by quasispherical magnetic ferroparticles with a characteristic size of ~100 Å, comparable with micelle dimensions. These experimental facts show Brochard and de Gennes' assumptions to be invalid. Measurements of the Fréedericksz transition [9,11] demonstrate the reorientation of the LC matrix in an external magnetic field. The critical field needed for reorientation, H_c, was ~10 Oe, two orders of magnitude lower than in pure LC's.

Our aim is to establish the physical mechanism of ferronematic reorientation in an external magnetic field. We now discuss some Fréedericksz transition results [9] in detail. Samples with thickness $D\sim100$ μm were used for measurements. The boundary condition at the cell surfaces was homeotropic, and all the samples had the director **n** aligned normal to the cell surfaces in the absence of an external magnetic field. It has been observed that strong fields (up to 400 Oe) applied in the cell plane have no reorientation effect. However, a relatively small field (~10 Oe) applied parallel to **n** distorted the LC matrix. The experimental data [9] for the critical field as a function of $D^{-1}\Phi^{-1/2}$ (D in micrometers) are shown in Fig. 1.

Berejnov *et al.* faced a serious problem in explaining their own data, because they took the Brochard–de Gennes ap-

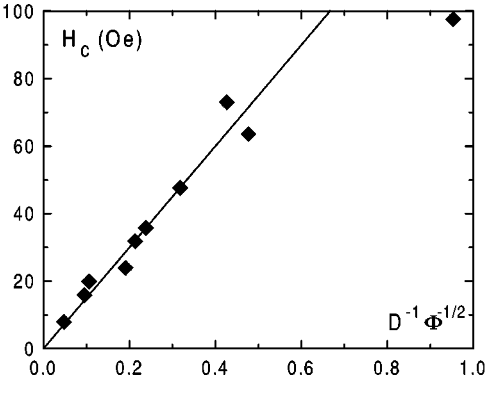

FIG. 1. Fréedericksz field as a function of variable $D^{-1}\Phi^{-1/2}$. Values of D are measured in micrometers. Diamonds are the experimental data points [9]. The solid line is calculated according to Eq. (7).

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proach and needed to assume strong coupling between LC micelles and the ferroparticle magnetic moment **m**. Since the mean size of magnetic grains is rather small, $\langle d\rangle \sim 100$ Å, they should be considered as superparamagnetic, meaning that the ferroparticle net magnetic moment **m** fluctuates within the particle. Therefore, there is no obvious reason for the coupling of magnetic and LC degrees of freedom, even admitting strong anchoring at the ferroparticle surface.

Here we digress to remind the reader that there are two mechanisms of ferroparticle magnetization relaxation in a liquid carrier: the Néel and the Brownian ones [14,15]. The Néel mechanism is related to the thermal fluctuations of the direction of the magnetic moment **m** *within* the particle itself. The characteristic Néel time τ_N of such processes is determined by the magnetic anisotropy K and equals $\tau_N = \tau_0 \sigma^{-1/2} e^{\sigma}$, where $\tau_0 \sim 10^{-8}$ s, $\sigma = K v_p / kT$, and v_p is the particle volume. The Brownian mechanism is due to magnetic moment rotation of the *whole* particle. The Brownian time τ_B depends on the fluid viscosity η as $\tau_B = 3\eta v_p / kT$. When the particle diameter is equal to the so-called Shliomis diameter d_S both times coincide, $\tau_N = \tau_B$. The Néel mechanism prevails when $d < d_S$. When $d > d_S$, the Brownian relaxation is dominant. The cases of soft (superparamagnetic) and rigid particles correspond to the conditions $\tau_N \ll \tau_B$ and $\tau_N \gg \tau_B$, respectively. Using the values of real ferrodispersion of $K = 1.34 \times 10^5$ erg/cm^3 [16], $\eta = 10^{-2}$ P, and $T = 290$ K we obtain for the Shliomis diameter $d_S = 150$ Å. Thus particles with a characteristic size ~ 100 Å have the Néel relaxation mechanism.

In order to overcome the above mentioned difficulty Berejnov *et al.* [9] assumed that the ferroparticle and micelle are coupled by a chemical bond such that the anisotropy axis of the magnetic grain falls in plane with a discotic micelle. Finally, after an additional assumption about the character of ferroparticle magnetic anisotropy, they achieved agreement with the experimental results.

We consider this explanation to be unnecessarily complex. A simpler and considerably more physical picture of this phenomenon can be drawn. In our opinion, there is no need to make any additional assumption about anchoring at the surface of ferroparticles.

We argue that the coupling of magnetic and LC degrees of freedom in ferronematics is *steric in nature*, arising from the anisometric shape of magnetically rigid (Brownian relaxation) ferroclusters. Let us clarify the last statement. The point is that in real ferrocolloids the magnetic components of ferronematics are polydisperse and there is some fraction of relatively big particles. It is well known (see, for example, the Monte Carlo data in [17,18] and the bibliography there) that for dipole-dipole interaction parameter values of $\lambda = m^2/d^3kT > 1$ these grains form aggregates: clusters of two, three, etc., particles. When $\lambda > 4$ and the concentration of magnetic grains is sufficiently high ($\Phi \sim 0.01$–0.1) ferrocolloids (i) loose aggregative stability, resulting in their decomposition into gaslike and liquidlike phases [17] or (ii) form very long (consisting of tens and hundreds of particles) chains of magnetic grains [19]. For volume fractions $\Phi < 0.001$ only clusters of a few particles form, which nucleate the future "liquid" or "chained" phases. Further, the formation of even dimers (cluster of two grains) causes a considerable increase of the effective value of the magnetic anisotropy K_{eff}. According to [20], this value is estimated to be $K_{eff} \sim 3M_s^2$, where M_s is the saturation magnetization of the ferroparticle material. Using values $M_s = 400$ G [9,16] or $M_s = 310$ G [12], we find that the effective magnetic anisotropy should be at least two times higher than that for a single particle (see above). As a result the value of the Shliomis diameter decreases from $d_S = 150$ Å to $d_S = 110$ Å. We estimate the characteristic size of the dimers as $d_{dimer} \sim 200$ Å. Since $d_{dimer} > d_S$, dimers should be considered as magnetically rigid Brownian particles. After adopting this picture of elongated small clusters of magnetic grains, a qualitative interpretation of the data in [9] becomes physically clear. In the absence of a magnetic field these elongated clusters are located between LC micelles due to steric micelle-grain interactions. An external magnetic field applied in the plane of the sample only stabilizes the initial LC texture. However, an out of plane magnetic field causes the clusters to realign in the field and distorts the LC matrix.

Now let us move to a quantitative analysis of the problem. We consider lyotropic ferronematics as a mixture of N_m discotic micelles of pure liquid crystal and N_f ferroaggregates. We suggest that the number of micelles is much higher than the number of magnetic particles, $N_m \gg N_f$ [11]. We approximate the shape of micelles by oblate ellipsoids of revolution with the semiaxes h and R playing the roles of half of the thickness and radius, respectively, of real micelles. Aggregates of ferroparticles are assumed to be prolate ellipsoids of revolution with long semiaxis a and short axis b. Both ferrodispersion and LC particles are supposed to be rigid and interact by steric repulsion only. Following the above estimations we assume that the Brownian relaxation mechanism dominates. We take into account these interactions in the spirit of Onsager's classical paper [21]. First, it is necessary to know the excluded volume $E(\mathbf{\Omega}_m, \mathbf{\Omega}_f)$ of two particles (micelle and ferroaggregate) with fixed orientations $\mathbf{\Omega}_m$ and $\mathbf{\Omega}_f$ of their symmetry axes. In order to calculate the excluded volume we followed the method in [22] developed for the case of equal ellipsoidal particles and made a straightforward generalization to different ellipsoids. The result for the excluded volume has the form of an expansion over even-order Legendre polynomials:

$$E(\mathbf{\Omega}_m, \mathbf{\Omega}_f) = \sum_{k=0} A_{2k} P_{2k}(\mathbf{\Omega}_m \cdot \mathbf{\Omega}_f). \tag{1}$$

Our calculation shows that the weight A_{2k} decreases rapidly as k increases for reasonable ratios $R/h < 10$ and $a/b < 10$. For example, the coefficient A_2 is approximately 30 times greater than A_4. Then, we retain in Eq. (1) terms up to second order only ($k = 1$). The most important coefficient for us, A_2, is equal to

$$\begin{aligned} A_2 = \frac{5\pi}{4} [& h b^2 (\Delta n_m - n_{m2} c_m^2)(\Delta \tilde{n}_f - \tilde{n}_{f2} c_f^2) \\ & + a R^2 (\Delta \tilde{n}_m + \tilde{n}_{m2} e_m^2)(\Delta n_f + n_{f2} e_f^2)], \end{aligned} \tag{2}$$

where the indices m and f denote the micelle and ferroaggregate, respectively; n_1 and n_2 are the demagnetizing factors of an ellipsoid of revolution along the symmetry axes and in the perpendicular direction; $\Delta n = n_2 - n_1; c > 1$ and $e < 1$ are the two eccentricities, defined in the usual way [23]. For example, for a micelle they are $c_m^2 = R^2/h^2 - 1$ and $e_m^2 = 1 - h^2/R^2$. Finally, the quantities with tildes denote the demagnetizing factors of a so-called additional or dual ellipsoid: for an oblate ellipsoid with eccentricity e (or c) this is a prolate ellipsoid with the same eccentricity e, and vice versa.

Next, let us obtain an expression for the magnetic part F of the free energy of the system. The magnetic susceptibilities of pure liquid crystal molecules and micelles are small [1,24] and we ignore them completely. The value of F is determined by the ferroaggregates only. The dimensionless magnetic part of the free energy $f = F/N_f kT$ per single ferroaggregate can be expressed as [21,25]

$$f = \int \Psi_f \ln \Psi_f d\mathbf{\Omega}_f - \xi \int (\mathbf{\Omega}_f \mathbf{h}) \Psi_f d\mathbf{\Omega}_f + N_m A_2 \int P_2(\mathbf{\Omega}_m \mathbf{\Omega}_f) \Psi_m \Psi_f d\mathbf{\Omega}_m d\mathbf{\Omega}_f . \tag{3}$$

Here $\Psi_f = \Psi_f(\mathbf{\Omega}_f)$ and $\Psi_m = \Psi_m(\mathbf{\Omega}_m)$ are the one-particle orientation distribution functions of ferroaggregates and micelles, respectively; $\xi = mH/kT$ is the Langevin parameter; and $\mathbf{h}$ is the unit vector along the magnetic field $\mathbf{H}$. Nematic order in the LC matrix is due to interactions between the micelles themselves. We are interested in calculating the Fréedericksz transition critical field only, i.e., just the onset of appearance of distortions of the LC matrix. Thus, it is possible to neglect the influence of the magnetic field on the distribution function of the micelles. After writing this distribution function as $\Psi_m(\mathbf{\Omega}_m) = \Psi_m(\mathbf{n} \cdot \mathbf{\Omega}_m)$ ($\mathbf{n}$ is the micellar director), and minimizing the functional (3), we find the orientation distribution function of ferroaggregates:

$$\Psi_f(\mathbf{e}) = Z^{-1} \exp[\xi(\mathbf{e} \cdot \mathbf{h}) - \sigma(\mathbf{e} \cdot \mathbf{n})^2]. \tag{4}$$

We defined $\mathbf{e} = \mathbf{\Omega}_f$ as the unit vector of the aggregate orientation; $Z = \int \exp[\xi(\mathbf{e} \cdot \mathbf{h}) - \sigma(\mathbf{e} \cdot \mathbf{n})^2] d\mathbf{e}$ is the normalization constant; $\sigma = 3\phi S A_2/(2v_m); \phi = N_m v_m/V$ is the volume fraction of micelles; v_m is the volume of a single micelle; V is the volume of the system; $S = \int P_2(\mathbf{n} \cdot \mathbf{\Omega}_m) \Psi_m(\mathbf{n} \cdot \mathbf{\Omega}_m) d\mathbf{\Omega}_m$ is the nematic order parameter.

This form of a one-particle distribution function was obtained in [9] after some unreliable assumptions concerning micelle-ferrocluster anchoring. Now we estimate the value of σ. Substituting the experimental data $h/R = 23/64$ we find that for $a/b < 10$ the value of σ is, with an accuracy of a few percent,

$$\sigma = \phi S \frac{b}{h} \left(0.11643 \frac{b}{h} + 0.52870 \right) \left(\frac{a}{b} - 1 \right). \tag{5}$$

Taking typical values of lyotropic liquid crystal parameters $\phi = 0.5, S = 0.6$ [24], the experimental data $2h = 23$ Å, and a characteristic value for the ferroaggregate axis $b = d/2 = 50$ Å, we determine $\sigma \simeq 1.35(a/b - 1)$. So, even for dimers this effective anisotropy is not small, $\sigma \simeq 1.35$. For a single quasispherical ferroparticle we obtain $\sigma = 0$. Therefore the dispersion of quasispherical ferroparticles cannot distort the LC matrix.

Now we calculate the Fréedericksz field needed for reorientation of our ferronematic. We assume that the external magnetic field is normal to the ferronematic cell as well as to the unperturbed director $\mathbf{n}_0$. Substituting Eq. (4) into Eq. (3) we find the density of the magnetic field dependent part of the free energy: $F_M = -n_f kT \ln Z$, where $n_f = N_f/V$ is the concentration of magnetic particles in the volume V. Then we follow the method given in [1]. Considering a small perturbation in the nematic director $\mathbf{n} = \mathbf{n}_0 + \delta \mathbf{n}$, we determine the variation of magnetic energy in the form

$$\delta F_M = -\frac{1}{2} n_f kT \xi^2 G(\sigma)(\delta \mathbf{n})^2,$$

$$G(\sigma) = \frac{1}{4} \left[2 - \frac{3}{\sigma} + \frac{6}{\sqrt{\pi\sigma}} \frac{\exp(-\sigma)}{\mathrm{erf}(\sqrt{\sigma})} \right]. \tag{6}$$

Here $\mathrm{er\,f}(x)$ is the error function. In writing Eq. (6) we used the condition $\xi < 1$ corresponding to the experiment [9]. The distortion energy δF_d is expressed via the elastic constant K_{LC} of the liquid crystal matrix and the thickness D of the cell [1] as $\delta F_d = \frac{1}{2}\pi^2 (K_{LC}/D^2)(\delta \mathbf{n})^2$. Finally, combining both energies we obtain the Fréedericksz field

$$H_c = \frac{\pi}{D} \sqrt{\frac{K_{LC}}{3\chi G(\sigma)}}, \tag{7}$$

where $\chi = n_f m^2/3kT$ is the initial susceptibility of the ferronematic.

In deriving Eq. (7) we implicitly assumed that all the aggregates are identical. We define the ratio a/b as the ratio of the long to the short ferroaggregate axis. Using the data $\chi = 0.6\Phi, H_c D \Phi^{1/2} = 150$ Oe$\times 1$ μm [9,12], and a typical value of the lyotropic elastic constant $K_{LC} \sim 10^{-6}$ dyn [24], and taking into account the estimation of Eq. (5), we find $\sigma \approx 0.2$ and $a/b \approx 1.14$. Thus, if all the magnetic clusters or grains in a ferronematic behave as Brownian particles, then their comparatively small effective anisotropy form will be sufficient to achieve the observed effect [9]. However, this result is not directly applicable to experimentally realizable ferronematics. We noted above that for real ferronematics [9] the ferroparticles are quasispherical, they have a polydispersity, and the Néel dominant relaxation mechanism. Next we extend the above calculation for such ferroparticles.

According to [9,12] the measured particle size distribution is log-normal $f(d) \sim (1/d) \exp[-\ln^2(d/d_0)/2s^2]$ with the parameters $d_0 = 82$ Å and $s = 0.3$. As stated earlier ferroparticles with $\lambda > 4$ definitely form aggregates. Let us divide the particle size distribution in two, one part containing particles likely to form clusters of two or more particles, $d > d_b = 154$ Å, and another monodisperse fraction, $d < d_b$. The subscript 2 refers to clustering, and 1 to monodisperse particles. After dividing the distribution we find magnitudes of the averaged grain sizes are $\langle d_1 \rangle = 84$ Å and $\langle d_2 \rangle = 172$ Å. The mean value of the large particle dipole parameter is

$\langle\lambda_2\rangle=4$, and for the small particle fraction $\langle\lambda_1\rangle=0.84$. Given this division the fraction of large particles is $\phi_2/\phi=0.018$. However, even such a small fraction contributes significantly to the initial susceptibility, $\chi_2/\chi=0.38$. This is well known [14,15] and derives from the fact that the initial susceptibility of a polydisperse ferrocolloid is proportional to the sixth moment of its distribution function, $\chi\sim m^2\sim\langle d^6\rangle$. Given the above estimation, large particles form primarily dimers. As we have seen, for a single magnetic grain the Shliomis diameter is $d_{1S}=150$ Å and for dimers it is $d_{2S}=110$ Å. As a result all small particles behave as Néel particles whereas large clusters behave as Brownian ones. Ferronematic reorientation is therefore due only to Brownian clusters. In this case we make the substitution $\chi\rightarrow\chi_2$. Recalculating using Eq. (5) gives $\sigma=3.14$ and $G(\sigma)=0.28$. Our calculated value for the Fréedericksz field as a function of $D^{-1}\Phi^{-1/2}$ is shown in Fig. 1 by the solid line. It corresponds to the value of the elastic constant of the LC matrix $K_{LC}=4.4\times10^{-6}$ dyn, which agrees with known data for pure lyotropic liquid crystals [24].

To summarize, the nature of the strong orientational effect in ferronematics is due to steric interactions between anisometric liquid crystal micelles and ferroparticle clusters. Our calculations show that even a small number of anisometric ferroparticles is sufficient to align the nematic director in an applied magnetic field. Additional experimental investigations into the internal structure of ferronematics would shed more light on this problem.

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