

Suspension of spherical particles in nematic solutions of disks and rods

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We report on the behavior of colloidal spheres suspended in nematic solutions of rodlike (calamitic phase) and disklike (discotic phase) micelles. The particles form anisotropic structures that depend on the shape of the surrounding micelles. An analysis of these structures indicates that dipolar and quadrupolar elastic interactions are, respectively, observed in discotic and calamitic nematics. This shape dependency can be understood by considering the entropy driven alignment of the micelles at the surface of the particles.

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At high volume fraction, disklike or rodlike particles in solution spontaneously align along a preferential direction [1]. The resultant mesophase is known as the nematic phase. It has an orientational axis specified by \mathbf{n} , a unit vector referred to as the director (\mathbf{n} is parallel to the normal to the disks, whereas it is parallel to the long axis of the rods). From disklike molecules [2] and rigid polymers [3] to anisotropic micelles [4,5] and rodlike viruses [6], numerous systems exhibit this organization. The stability of this phase can be understood by just considering hard core interactions between the anisotropic objects (nematogens). In these conditions, the free energy of the system includes only entropic contributions [1,2,7]. At high volume fraction, the entropy of the system is higher in the ordered phase than in the isotropic one, the loss of rotational entropy in the nematic state being compensated by the reduction of the excluded volume of the nematogens. Hard-core interactions and the resultant entropic effects also play an important role in the behavior of colloidal spheres suspended in solutions of smaller isotropic or anisotropic particles. The overlap of excluded volume of small particles around large spheres leads to an isotropic attraction known as the depletion interaction [8]. The problem is expected to be richer in more concentrated solvent in which small anisotropic particles form a nematic matrix that can be considered as a continuum [1,2] with respect to the larger spheres. In such systems, the entropy of the hard-core particles should govern the alignment of the nematogens both in the bulk and at the interface of the colloidal particles [9]. As sketched on Fig. 1, the excluded volume of a disk or a rod at a surface is reduced when the particle is parallel to the surface. Again, this reduction of excluded volume is accompanied by a loss of rotational entropy. This latter contribution being weaker, rodlike and disklike nematogens are expected to align parallel to a surface [9]. Consequently, the associated director should exhibit normal or parallel orientation with respect to the surface leading to distinct distortions of the nematic order around spherical particles. Due to the elastic cost of these distortions [10], the particles should experience different elastic interactions and self-organize into dissimilar spatial structures.

In this paper, we aim to identify these structures in order to extend our understanding of the basic behaviors of systems simply governed by hard-core interactions. For this purpose, we study the behavior of latex spheres suspended in lyotropic liquid crystals composed of disklike or rodlike sur-

factant micelles. The interactions between the micelles as the interactions between the micelles and the latex spheres are mostly of the hard-core type, making this system a good model to test the behavior of spheres in nematic solutions of disks and rods.

Using optical microscopy, we show the existence of anisotropic interparticle interactions mediated by the nematic matrix. The observed colloidal structures have different symmetry in disklike or rodlike micellar solutions. Considering a continuum description of the nematic state [1,2], the interactions between the particles can be ascribed to the orientational elasticity of the micellar solution. Moreover, using an electrostatic analogy [10,11], we deduce that the spherical particles experience dipolar elastic interactions in discotic phases and quadrupolar elastic interactions in calamitic phases. These interactions reflect different anchoring conditions and show that the associated surface energies overcome the elastic cost of the distortions.

The lyotropic liquid crystal is a ternary mixture composed of sodium dodecyl sulfate (SDS), decanol (DeOH), and water. The phase diagram exhibits both calamitic (N_C) and discotic (N_D) nematic domains [4]. We have chosen two compositions in these domains: N_D (water, 66.1%; SDS, 28.2%; DeOH, 5.7% by weight); N_C (water, 68.9%; SDS, 26.1%; DeOH, 5.0% by weight). We point out that these two compositions are very close. Therefore, although being differently shaped, the micelles have almost identical interfacial properties. We can assume that in both systems the interactions are of the hard core type because the electrostatic repulsion is strongly screened due to the high ionic strength of the solutions [12]. The nature of the phases is deduced from polarizing microscope observations of thin samples confined between glass slides separated by about 20 μm . Indeed, in

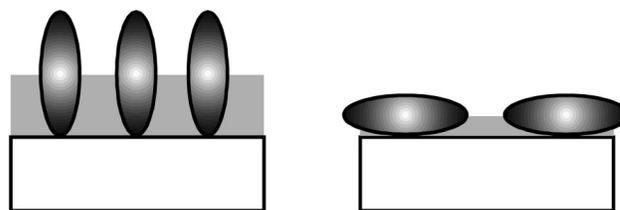


FIG. 1. Anisotropic particles (rodlike or disklike) close to a wall. The excluded volume that is sketched by the gray area is smaller when the particles align parallel to the surface.

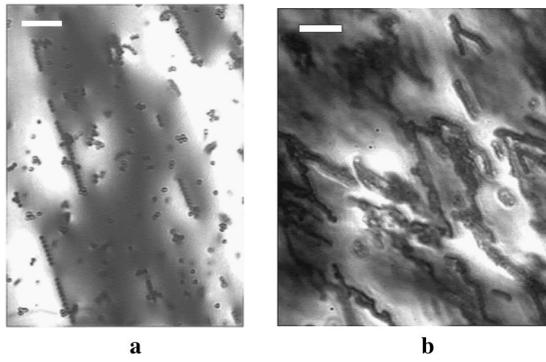


FIG. 2. Optical microscope pictures of 1.4- μm latex particles in surfactant nematic phases. The samples are observed between crossed polarizers and contained in sealed 100- μm -thick rectangular capillary tubes. White bar: 15 μm . (a) Discotic nematic phase (N_D): the particles form long parallel chains. (b) Calamitic nematic phase (N_C): the particles form more compact anisotropic clusters and V structures.

the N_C phase, the micelles and the associated nematic director spontaneously align parallel to the slides. Such alignment is known as planar anchoring and can be detected by rotating the sample with respect to the crossed polarizers [13]. In the N_D phase, the alignment of the micelles leads to homeotropic anchoring with the director normal to the slides. As a result, the sample is dark between crossed polarizers regardless of their relative orientation. 1.4 micron latex particles were introduced in the samples at a volume fraction of approximately 1%. The nature of the nematic phases is not affected by the presence of particles at such low volume fraction. However, due to the elastic distortions induced by the particles, a demixtion is expected at equilibrium with a complete segregation between the nematic phase and the particles [5]. To avoid this segregation and suspend the latex spheres within the nematic phase, the samples are vigorously shaken.

As shown on Figs. 2(a) and 2(b), the particles organize into well-defined anisotropic structures within the nematic. The structures are stable over several days meaning that they are stabilized by both attractive and repulsive interactions between the colloidal spheres. In fact, such interactions arise from the orientational elasticity of the solvent and clearly depend on the nature of the nematic phase. Although observed in 100- μm -thick capillary tubes in which the global nematic alignment cannot be controlled, the particles form chainlike structures in the N_D phase whereas they form more compact clusters in the N_C phase. By contrast with aggregates resultant from segregation [5], these clusters are anisotropic with connected chains in V-shaped arrangements. In order to fully characterize the anisotropy of the clusters with respect to the nematic director we also observed the systems in thinner samples and at the wedges of capillary tubes.

The microscope picture of Fig. 3(a) shows linear chains normal to the wedge of a rectangular capillary tube in the N_D phase. In this region of the sample, the nematic director is locally normal to the capillary wall. Therefore, we deduce that the long chains observed in the N_D phase are aligned along the nematic director. We have observed a similar behavior in the N_D phase of the water/perfluorooctanoate mixture [14], confirming that this effect is independent of the

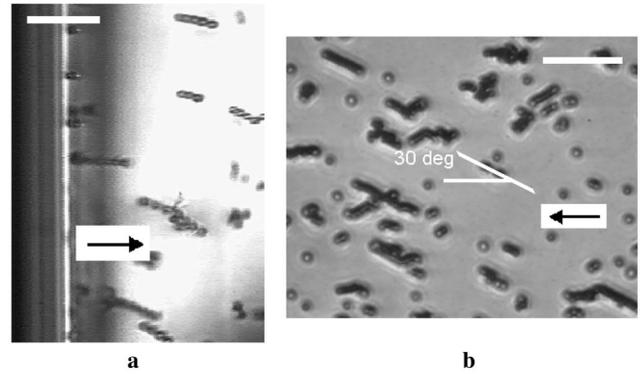


FIG. 3. (a) Optical microscope picture of 1.4- μm latex particles in the N_D phase at the wedge of a rectangular capillary tube. Close to the wall, the nematic director is normal to the wedge as indicated by the black arrow. Further away from the wedge, the orientation of the director changes due to the competition between the orientation induced by the wedge (indicated by the arrow) and the one induced by the upper and lower flat walls of the capillary tube (perpendicular to the plane of the picture). In the vicinity of the wedge, the chains are clearly oriented parallel to the director. White bar: 15 μm . (b) Optical microscope picture of 1.4- μm latex particles in the N_C phase between glass slides separated by approximately 20 μm . The director is parallel to the slides and its orientation is indicated by the black arrow. The angle between the global nematic alignment and a line joining the center of two adjacent particles can be positive (approximately $+30^\circ$) or negative (approximately -30°). In two dimensions, this results in the formation of distorted chains with the average orientation going from 0° to about plus or minus 30° for the largest angles. White bar: 15 μm .

system chemistry. The formation of chains suggests that the particles experience dipolar elastic interactions as recently reported for thermotropic liquid crystals in conditions of strong normal anchoring [11]. This electrostatic analogy arises from the minimization of the elastic free energy [1]: $E_{el} = \int_V \frac{1}{2} [K_1(\text{div}\mathbf{n})^2 + K_2(\mathbf{n} \cdot \text{curl}\mathbf{n})^2 + K_3(\mathbf{n} \times \text{curl}\mathbf{n})^2] dV$, where K_1 , K_2 , and K_3 are the nematic elastic constants. Assuming a single elastic constant [1,10], the components of the nematic director are expected to be solutions to the Laplace's equation. The lowest-order term and the resultant far field behavior are set by the symmetry of the distortions around the particles. As shown on Fig. 4(a), a dipolar configuration with a vector symmetry is predicted and observed

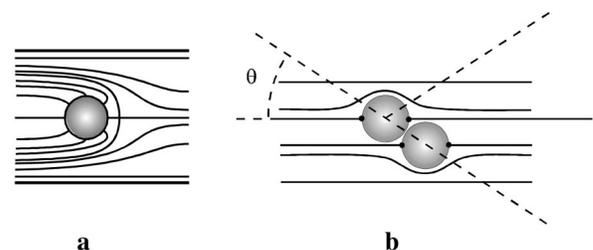


FIG. 4. Schematic of the director field around a colloidal particle. (a) Normal boundary conditions: the dipolar configuration has a hedgehog defect. (b) Planar boundary conditions: the quadrupolar configuration has two boojums surface defects. The line joining the center of two particles adopts an angle of $\theta=30^\circ$ with respect to the nematic alignment in order to minimize the elastic distortions.

in conditions of normal anchoring at the surface of the particles [10,11]. This configuration includes a topological defect known as a hedgehog defect. It allows the topological constraints that the director must be normal to the particle surface and globally aligned far from the sphere to be satisfied. The first constraint indicates that any deviation from the normal anchoring conditions has an energetic cost that is dominant in this problem. Such deviations would allow less distorted configurations with lower elastic cost [14,15]. The surface energy of a deviation can be estimated using a simple dimensional argument. Having an entropic origin, it is on the order of $k_B T/a^2$ per unit surface where $k_B T$ is the thermal energy and a a typical micellar size (about a few nanometers [4]). The total surface energy is thus approximately $R^2 k_B T/a^2$, where R is the radius of the spherical particle. The other energetic contribution corresponds to the bulk elastic distortions. It is on the order of KR . Since K is approximately $k_B T/a$ [1], the ratio of the elastic contribution over the surface energy is typically a/R . The spheres being much larger than the micelles, one deduces that the surface energy is much larger than the elastic one. This explains the absence of deviations from normal anchoring. Therefore, our observations confirm that the disks are parallel to the particle surface as expected from minimization of the excluded volume of the micelles [9].

The microscope picture of Fig. 3(b) shows latex particles in the N_C phase confined between two glass slides separated by approximately $20 \mu\text{m}$. In such thin samples, the nematic alignment is parallel to the slides and the clusters are quasi-bidimensional. We observe chains which adopt nonzero angles with respect to the nematic alignment. We plot on Fig. 5 the magnitude of the largest angles measured for a serie of long chains. Analysis of several pictures shows that they are roughly equal to plus or minus 30° . Such anisotropy reflects the quadrupolar character of the nematic distortion around the particle and of the resultant elastic interaction [11]. A quadrupolar configuration is expected in conditions of strong planar anchoring as shown on Fig. 4(b). This configuration includes two surface defects that are diametrically opposed and located at the poles of the particle (boojums defects). As in the previous case, the surface energy largely exceeds the bulk elastic one, leading thereby to the strength of the present anchoring. To minimize the elastic distortions, the line joining the center of two droplets makes a 30° angle with respect to the global nematic alignment. Consequently, in two dimensions, the formed chains exhibit this particular angle. However, this also allows the formation of more dis-

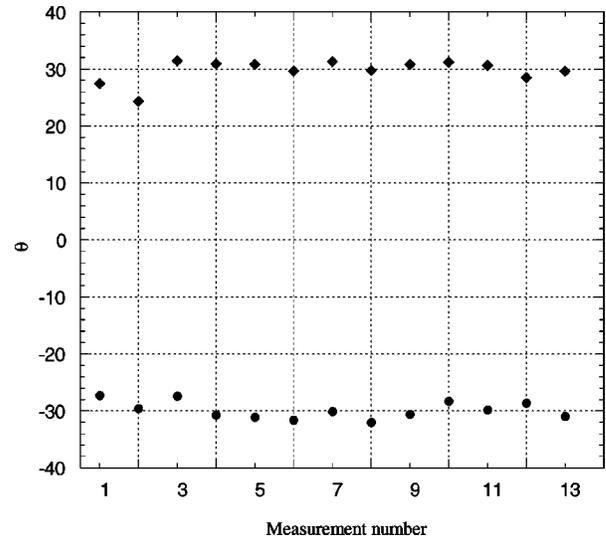


FIG. 5. Magnitude of the largest angles between the director and long chains of particles measured on several microscope pictures similar to that of Fig. 3(b). Positive and negative values are plotted as functions of the measurement number. We find approximately the same number of positive and negative values, as expected from the symmetry of the nematic phase. The average angles are equal to $+$ or -30° .

torted structures as this angle can change its sign from one droplet pair to another one. This explains the presence of elongated structures that adopt a lower effective angle with the director. Again, as deduced for the N_D phase, investigations of the N_C phase confirm that the micelles are parallel to the particle surface. In this case, the alignment leads to planar anchoring and quadrupolar interactions instead of normal anchoring and dipolar interactions.

We have demonstrated that entropic effects can lead to specific ordering of spherical particles suspended in nematic solutions of rods or disks. Moreover, this ordering can be controlled through the shape of the surrounding objects. In solutions of disks, the spheres experience dipolarlike interactions leading to the formation of long chains. In solutions of rods, the spheres experience quadrupolarlike interactions leading to the formation of more compact anisotropic clusters. Our results extend previous findings concerning mixtures of small spheres and long rods [6]. These phenomena are very general since hard-core interactions are ubiquitous. Also, a wide variety of phases and organizations is still expected with changing the size, the shape and the concentrations of anisotropic or isotropic hard-core particles.

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