Liquid Crystal Formation in Suspensions of Hard Rodlike Colloidal Particles: Direct Observation of Particle Arrangement and Self-Ordering Behavior

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We successfully prepared monodisperse, hard rodlike colloidal particles with a wide range of length-to-width ratios (L/W). In their suspensions liquid crystals, or nematic (N) and smectic (Sm) phases, spontaneously appeared. The size of the particles made it possible to directly observe their arrangement and dynamics with an optical microscope. The phase behavior observed exhibited an I (isotropic)-Sm transition for $L/W = 3.5$–8.0 and I-N-Sm transitions for $L/W = 10$–35. In pre-Sm transition regions, lateral clustering of the particles and subsequent layering of the clusters were observed exactly.

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Orientationally and/or positionally ordered phases frequently appear in a variety of suspensions of rodlike colloidal particles. In fact, beautiful iridescent phases have been observed in suspensions, e.g., of inorganic particles, β-ferric oxyhydroxide (FeOOH) [1–5], and rodlike viruses (tobacco mosaic viruses, TMV) [6]. By preparing monodisperse β-FeOOH particles [3–5] and isolating the monodisperse TMV particles [6–11], the iridescent colors were shown to be due to layered (smectic) or crystalline structures of the particles. Ordered structures were also found in systems of colloidal rods of V_2O_5 [12] and γ-AlOOH [13], and semiflexible rodlike molecules, e.g., DNA and bacteriophage fd (see Ref. [14]), and collagen [15,16].

Onsager's theory [17] showed that systems of long hard rods interacting with purely repulsive forces exhibit an orientational (or nematic) order at critical densities far from the closest packing. Computer simulations have further shown that systems of hard spherocylinders (HSC), interacting with hard-core steric repulsions, exhibit not only the N phase but also cholesteric, Sm, columnar, and crystalline (C) phases [18–22]. Moreover, phase diagrams for these HSC systems have been calculated as a function of density and shape-anisotropy (L/W), where the existence of two triple points has been predicted [21,22].

The interaction between real colloids, however, consists of both electrostatic repulsive forces due to the overlap of electrical double layers and of attractive van der Waals forces. According to the Derjaguin-Landau-Verwey-Overveek theory [23], the stability of colloid suspensions depends on the balance between these two forces. At low ionic concentrations the electrostatic repulsion is dominant, and thus the colloid-colloid interactions can be approximated by the sum of hard-core and electrostatic (soft) repulsions. Onsager's theory is applicable to such repulsive particle systems, if the bare particle diameter is replaced by an effective (increased) diameter [9,14,17]. However, at high ionic concentrations, the interparticle potential curve has a secondary minimum [23], and this can also generate reversible ordered aggregations of the particles resulting from a condensation-type phase separation (e.g., liquid → solid) at lower densities [24].

Compared with such theoretical advances, experimental works have been pretty much outdistanced. So far, the only real systems forming the smectic phase (which is the most highly ordered mesophase) which have been reported are systems of β-FeOOH [3–5] and TMV [10,11] particles. However, their L/W values are limited to a single value, approximately 5 and 17, respectively. Thus, to experimentally evaluate the phase diagrams predicted by computer simulations of HSC systems [21,22], hard rod systems with a wide range of L/W are needed. In the present study, we have successfully prepared a series of monodisperse colloidal rods [β-FeOOH, selenium (Se), and nickel dimethylglyoxime (NDG)] with a range of L/W between 3.5 and 35 and directly observed ordering behavior of the rods exhibiting active Brownian motions. Our observation system consists of an inverted-type optical microscope and a 7°-tilted [3], by which all the density-dependent phase structures can be together observed as shown in Figs. 1–4.

Smectic ordering for particles with $L/W = 3.5$.—Monodisperse, rodlike colloidal particles of Se with $L = 0.82 \pm 0.14\ \mu\text{m}$, $W = 0.23 \pm 0.02\ \mu\text{m}$, and $L/W = 3.5$ were prepared by adding hydrazine solutions of metallic selenium to water. The Sm ordering process in Se suspensions with low ionic concentrations of $(10^{-4}$–$10^{-5})M$ (where the particles repulsively interacted with one another) was viewed with an optical microscope. The individual particles were clearly observed to exhibit quick translational and rotational Brownian motions in I regions. At densities high enough to drastically restrict the Brownian motions of the particles, particularly rotational ones, small clusters of the particles aligning side by side

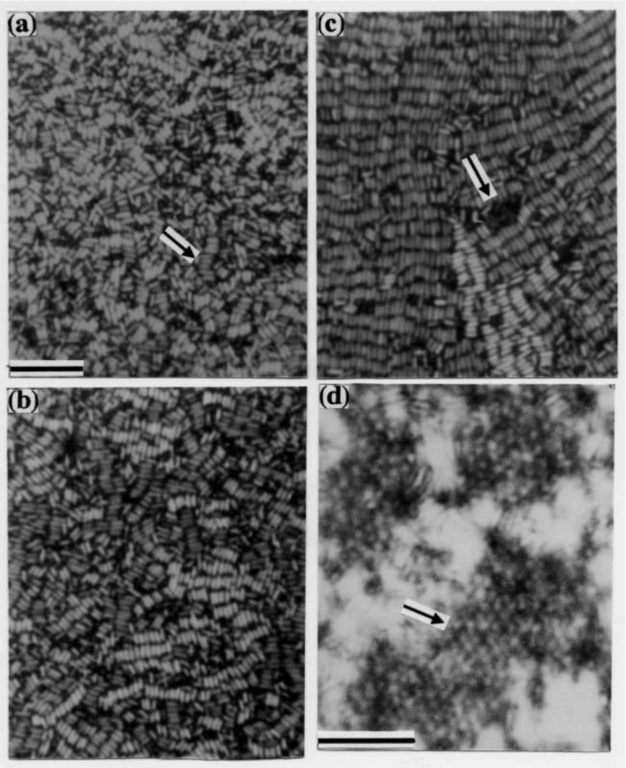

FIG. 1. (a) Transient clusters of typically 5–10 particles aligning side by side (e.g., shown by the arrow) for a Se suspension (the scale bar: 5 μm). (b) The numbers of the clusters increased with particle density, and then layering of 2–5 clusters occurred locally. The scale bar for (a) is the same as for (b) and (c). (c) An Sm region covered with the grown clusters. In the dark regions (e.g., shown by the arrow), only the ends of the particles were actually observed. (d) An arrangement of the particle ends (light dotlike entities) in a dark region of a Sm layer (the scale bar: 3 μm).

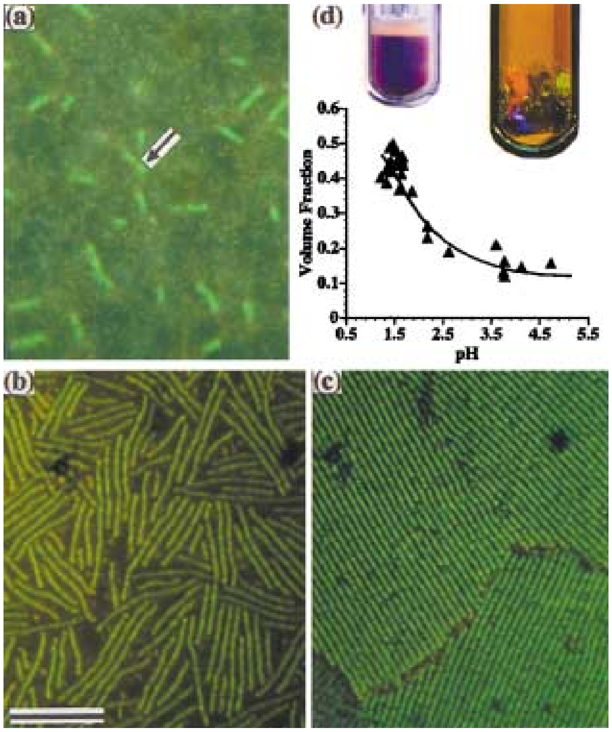

FIG. 2 (color). (a) The single particles (small light dot, $L = 0.644$ μm and $W = 0.137$ μm) and a separated dense phase (light wormlike ones, the arrow) for a FeOOH suspension kept in a space less than 5 μm thick [the scale bar for (b), 10 μm, is the same as for (a) and (c)]. (b),(c) Particle ordering for a β-FeOOH suspension; (b) many stringlike entities or the side of matlike 2D assemblies of the particles (2–25 μm in side length) in a high density region. (c) Four neighboring Sm domains (with a layer thickness of 0.76 μm) at a higher density. (d) The pH dependence of the critical (minimal) volume fraction η of the β-FeOOH particles for the Sm phase formation. Two glass test tubes, respectively, containing β-FeOOH suspensions with pH 1.34 (attractive: left) and 4.1 (repulsive: right), exhibit I(upper)/Sm(lower, iridescent) phase separation.

appeared here and there but soon collapsed thermally or by collision with the surrounding particles. The clusters of 5–6 particles had lifetimes of approximately 1 sec or less. As the particle density increased, moreover, the clusters grew laterally and the lifetimes lengthened. Then, as the number of clusters increased, double-, treble-, and multiple layering of the clusters occurred, finally resulting in widely extended Sm layers (without going through the N phase). In fact, Fig. 1 shows snapshots of pre-Sm transition regions appearing in a Se suspension with an ionic concentration of $1.4 \times 10^{-5} M$, where clusters of typically 5–10 particles [e.g., shown by the arrow in Fig. 1(a)], the layers of more developed clusters [Fig. 1(b)], and a resultant Sm region [Fig. 1(c)] are visible. Computer simulations for HSC systems [21,22] predicted that the Sm phase is stable at L/W values above 4.1–4.2 where the I-Sm-C triple point is located. An increase in the effective width of the Se particles due to repulsions further decreases the L/W ratio of 3.5. However, such a decrease is explainable if stronger repulsions can more largely depress the orientational fluctuation of the particles. We have found an orientational depression effect with NDG particle suspensions having various ionic concentrations.

The lateral arrangement of the Se particles in Sm layers was also observed with an optical microscope. Figure 1(d) shows a Sm layer, viewed from the particle alignment direction, that appeared in a Se suspension with an ionic concentration of $1.4 \times 10^{-5} M$, where many light spots (e.g., shown by the arrow) are visible, corresponding to the ends of the individual particles. The array of the ends locally revealed hexagonal latticelike packing with a period of 0.32–0.46 μm, suggesting the onset of a phase transition from Sm-A to Sm-B at a higher particle density. For a HSC system, Frenkel predicted the possibility of a Sm-A to Sm-B transition in his simulation [20]. For TMV particles, a liquidlike arrangement in the Sm [10] and hexagonal packing in the crystals [8,10] were observed with x-ray scattering.

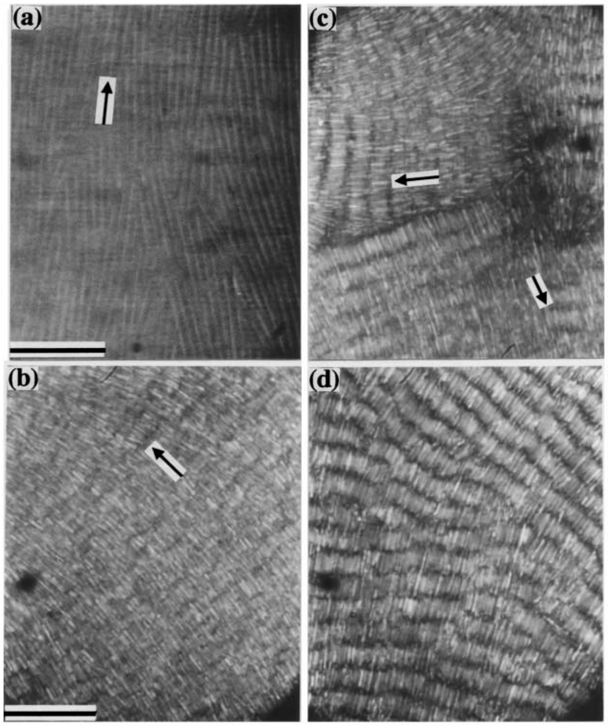

FIG. 3. (a) Arrangement of the particles (light needlelike entities) in an N phase for a NDG31 suspension (the scale bar: 5 μm). (b)–(d) Pre-Sm regions for a NDG10 suspension; (b) a widely extended N region, where local end matching of the particles (the arrow) is seen here and there. The scale bar, 10 μm, is the same as for (c) and (d). (c) Double and treble layering of the laterally grown, clear-cut clusters (the arrows) in an N region. (d) A Sm structure at a further higher density region.

Smectic ordering for particles with $L/W = 4.4$–8.0.—Highly monodisperse rodlike colloidal particles of β-FeOOH with standard deviations of $L < 4.5\%$ and a L/W range from 4.4 to 8 were prepared from ferric chloride aqueous solutions. Some examples of the mean dimensions of the particles used, $L \times W$ μm^2 (L/W), are $0.27 \times 0.06(4.5)$, $0.644 \times 0.137(4.7)$, $0.358 \times 0.062(5.8)$, and $0.581 \times 0.072(8.0)$. For the β-FeOOH particles, the ion determining the surface potential is the proton. The Sm ordering mechanism at low pH was found to be different from the one at high pH where electrostatic repulsion is dominant. Considering the results of computer simulations for the HSC systems [18–22] together with Onsager's theory [17], smectics for repulsive rods may be induced by excluded volume effects of the rods [as in Figs. 1(a)–1(d)]. However, for high ionic (protonic) concentrations, the interparticle potential curve has a secondary minimum, which can induce a condensation-type phase separation at lower densities [24] where the excluded volume effect is ineffective. Figure 2(a) shows an isotropic phase of many single β-FeOOH particles exhibiting active Brownian motions (small light dots) and a separated dense phase (light wormlike entities, which are clusters of the particles aligning side by side and which also exhibited active Brownian motions) for a β-FeOOH suspension with pH 1.7. The particles at each cluster edge were observed to repeatedly go in and out. The particle density in the isotropic phase was significantly low, suggesting that the wormlike clusters can be stabilized (not by excluded volume effects) probably by the balance between attractive van der Waals forces and electrostatic repulsive forces. With increasing density of the attractive particles, more clusters appeared, grew, recombined, and finally layered to form Sm structures without going through the N phase. In fact, Fig. 2(b) shows many stringlike entities appearing in a β-FeOOH particle suspension with $p\text{H} = 1.9$. These strings are actually the sides of matlike 2D assemblies (clusters) extending perpendicular to this image, where the particles oriented almost perpendicular to the assembly plane. The assemblies unceasingly exhibited thermal fluctuations in various modes. Around the assemblies the single β-FeOOH particles and their small clusters were present, exhibiting quick Brownian motions. As density increased the assemblies were packed more closely and finally formed widely extending Sm layers [Fig. 2(c)].

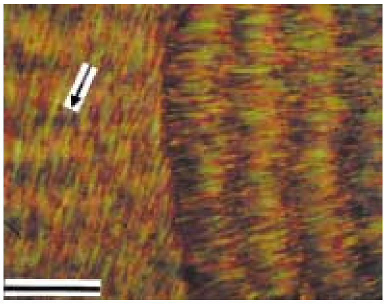

FIG. 4 (color). Sm and pre-Sm regions in the N phase for a NDG35 suspension. The boundary line near the center of this image is an N-N interface already appearing in the N phase (the scale bar: 10 μm).

The volume (or packing) fraction η of the β-FeOOH particles in the Sm phase was found to strongly depend on suspension pH. Moreover, the fraction gradually or noticeably increased in the Sm phase with lowering height level from the phase boundary. Figure 2(d) also illustrates the pH dependence of the critical (minimum) packing fraction required for the onset of the Sm phase (approximated by the η value averaged over the Sm region 2 mm thick just below the phase boundary). The η value shows a nonlinear decrease from 0.45 to 0.14 with increasing pH, which may be mainly due to an increase in the excluded volumes of the particles with increasing pH. Extension of this curve to low pH seems to approach the packing fraction for HSC systems predicted by computer simulations [21,22].

Ordering for particles with $L/W = 10$–35.—By mixing aqueous solutions of dimethylglioxime and nickel acetate, we synthesized monodisperse rodlike colloidal nickel dimethylglioxime (NDG) particles with four distinct dimensions, ($L = 2.40 \pm 0.31\ \mu$m, $W = 0.23 \pm 0.02\ \mu$m, $L/W = 10.2$), (5.00 ± 0.30, 0.29 ± 0.07, 17.4), (4.74 ± 1.00, 0.15 ± 0.04, 31.4), and (5.80 ± 1.00, 0.13 ± 0.05, 35.4). They are called here NDG10, NDG17, NDG31, and NDG35, respectively. Below an ionic concentration of $1 \times 10^{-2} M$, nematic regions eventually increased in the I phase with increasing density, and finally a widely extended Sm phase was observed. An example of the particle arrangement in the N phase is shown in Fig. 3(a). The N phase was induced by dilution from the Sm phase formed in a NDG31 suspension with an ionic concentration of $1.08 \times 10^{-4} M$. Individual particles are clearly seen to orient approximately in the direction along the arrow, but not to form any layers.

The Sm ordering process in the N phase was also visualized with an optical microscope. For example, the snapshots of the process for a NDG10 suspension with an ionic concentration of $4.2 \times 10^{-3} M$ are shown in Figs. 3(b)–3(d). Figure 3(b) shows a widely extended N region, where the particles oriented almost parallel to the direction indicated by the arrow. Small clusters of the particles matching their ends also appeared here and there in the N phase (e.g., shown by the arrow), although the contour of the clusters was still fuzzy. Such clusters likely correspond to the Sm precursor suggested by Frenkel in his computer simulation [20]. As the particle density increased, the clusters grew laterally, the contour became clearer, and the double, treble, and more layering of the clusters appeared eventually. Figure 3(c) shows double and treble layers of the grown cluster (the arrows) and local fuzzy pre-Sm layering (around the top and bottom) in the N phase. Figure 3(d) shows a widely extended Sm region appearing in a further denser region. The computer simulations [21,22] predicted a critical (minimal) L/W ratio of 4.7–5.0 for the stable N phase (where the I-N-Sm triple point is located). However, the N phase was not observed for the β-FeOOH particles, whose L/W ratios are 4.4–8.0. Neither was it observed in suspensions of γ-AlOOH particles with a mean L/W ratio of 8 [13]. Such L/W ratios for these colloids, being somewhat larger than those for the HSC, will become less by considering their effective widths due to repulsions. Also, a polydispersity of the particle lengths, still existing, could be one of the causes of the difference. The Sm layer period (thickness) and in-layer particle separation were measured to be 2.9 and 0.34 μm, respectively, for a NDG10 suspension with $4.2 \times 10^{-3} M$. From these values the particle packing fraction η of the Sm phase was estimated to be 0.4. This value will be closer to the η value of 0.45 predicted by computer simulations [21,22], if the effect of electrostatic interactions is considered.

Figure 4 shows a Sm region appearing in the N phase for a NDG35 suspension with an ionic concentration of $1.0 \times 10^{-2} M$. In the right side region, Sm layers were clearly recognized, while in the left side region the particles are well oriented and show the N phase with fuzzy pre-Sm layers (the arrow). For TMV suspensions, Sm-like density fluctuations were observed in the N phase with static light scattering [10], and the dynamics of the fluctuations were further investigated with dynamic light scattering [11].

In summary, by preparing a series of hard, monodisperse colloidal rods with a wide range of L/W, we have directly observed the self-ordering process of rods and resultant liquid crystalline structures in suspensions. The strongly shape-anisotropy dependent phase behavior that we found basically agrees with the predictions by computer simulations. We expect that our colloidal systems can serve not only as a reference for such theoretical approaches but also as a visualized model of real systems with small rodlike molecules to study their phase behavior.

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