nature of dependence of particle diffusion properties on surface functionalization.

## II. EXPERIMENT

### A. Materials and sample preparation

We used a single-compound room temperature nematic LC 4-pentyl-4-cyanobiphenyl (5CB) from Frinton Laboratories, Inc., as a host for gold NPs of different anisotropic shapes, dimensions, and surface properties (Table I). Elongated convex pentagonal (CPNs) and con-

TABLE I. (Continued)

| | Nanoparticle and director fields | Dimensions (nm) 2R | L | Surface anchoring/ Director configuration | $D_a$ ($\mu m^2/s$) | $D_b$ ($\mu m^2/s$) | $D_a/D_b$ | $D_{\parallel}$ ($\mu m^2/s$) | $D_{\perp}$ ($\mu m^2/s$) | $D_{\parallel}/D_{\perp}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Isotropic colloidal particle in anisotropic host | Elastic dipole | | | | | | | | | |
| | | 35 | 35 | Homeotropic/ Dipolar | – | – | – | $4 \times 10^{-2}$ [27][c] | $2.7 \times 10^{-2}$ [27][c] | 1.64 [39][d] 1.48 [27][c] |
| | Homeotropic elastic quadrupole | | | | | | | | | |
| | | 35 | 35 | Homeotropic/ Saturn ring | – | – | – | $5.6 \times 10^{-2}$ [27][c] | $3.67 \times 10^{-2}$ [27][c] | 1.72 [39][d] 1.53 [27][c] |
| | Planar elastic quadrupole | | | | | | | | | |
| | | 169 | 169 | Tangential/ Bipolar | – | – | – | – | $6.28 \times 10^{-2}$ [25][c] | 2.18–3.02 [33][d] 2.2–2.5 [63][c] |
| | Uniform | | | | | | | | | |
| | | 35 | 35 | Tilted/ Uniform | – | – | – | – | – | [39][d] |

[a]Data for different orientations; see Figs. 1(c) and 1(d).
[b]Estimated using Eqs. (5) and (6).
[c]Experimental measurements.
[d]Numerical simulations.

of incident light and often allows one to deduce the actual orientation of such NPs [29,44].

CPNs have homeotropic anchoring on their surfaces (Table I) and align with their long axis a perpendicular to a substrate surface rubbing defined far-field director orientation $\mathbf{n}_0 = \{0, 0, 1\}$ [Fig. 1(a)]. The symmetry of resulting director distortions $\mathbf{n}(\mathbf{r})$ around CPNs [Fig. 1(a)] is of "quadrupolar" type [3,6,27], with encircling half-integer disclination loop (often called "Saturn ring") [26,29] of winding number $-1/2$. CPN drifts in the plane of the liquid crystal cell due to Brownian motion. The typical erratic trajectory obtained from 4300 frames of video tracking of CPN is shown in Fig. 1(b). At the same time, CPN can also freely rotate around its transverse (short) axis $c(\|\mathbf{n}_0)$ [Fig. 1(a) and insets in Figs. 1(c) and 1(d)]. Using dark-field video microscopy tracking data, one can construct a histogram of displacements $\Delta = r(t + \tau) - r(t)$ (Fig. 1), translational or rotational, NP makes from the frame to frame over the elapsed time $\tau$ [8,25,27,40]. In experiments $\Delta$ was measured in $x(\perp \mathbf{n}_0)$, $y(\perp \mathbf{n}_0)$, $z(\|\mathbf{n}_0)$, a, or b directions for translational diffusion and due to angle $\theta$ changes for rotational diffusion (note that the symmetry of the LC-NP composite with NPs following director orientation states in the LC host is uniaxial). As expected, experimentally obtained displacement distributions (Fig. 1) can be fit by a Gaussian function of the form [8,25,27,40]

$$P(\Delta|\tau) = P_0(\Delta)\exp[-\Delta^2/(4D\tau)], \qquad (1)$$

where $P(\Delta|\tau)$ is the probability that over the time $\tau$ a nanoparticle will displace by $\Delta$, $P_0(\Delta)$ is a normalization constant, and a value $4D\tau$ determines the width of the distribution [40,51], where $D$ is a diffusion coefficient and the subscript indices $= \|, \perp$ stand for translational diffusion along and perpendicular to $\mathbf{n}_0$, respectively, indices $=$ a, b stand for translational diffusion along longitudinal and transverse axes of the axially symmetric anisotropic NP, respectively, and $= \theta$ for rotational diffusion around c. The larger width of distribution defines a larger diffusion coefficient. Figures 1(c) and 1(d) show displacement distributions of the CPN nanoprism in the planar cell. The difference in width of distributions [Fig. 1(c)] corresponding to two orthogonal directions indicates that the diffusion of CPNs is anisotropic with respect to $\mathbf{n}_0$. Interestingly, this anisotropy also depends on the orientation of the CPN while it freely rotates around $\mathbf{n}_0$, with respect to the plane of the cell (in the plane orthogonal to $\mathbf{n}_0$). When a is roughly parallel to the plane of the cell [Fig. 1(c)], the diffusion in the direction normal to $\mathbf{n}_0$ is easier than along $\mathbf{n}_0$ ($D_{\|}/D_{\perp} < 1$), but diffusivity anisotropy switches to $D_{\|}/D_{\perp} > 1$ when a is

FIG. 1. (Color online) Diffusion of CPN nanoparticle in a nematic liquid crystal. (a) Schematic diagram of CPN and surrounding director Þeld $\mathbf{n}(\mathbf{r})$ (thin blue lines); a thick red line around NP shows a disclination loop. (b) Trajectory of Brownian motion in the planar cell ($d$  3 μm). (c), (d) Histograms of displacements along ($z$ axis) and perpendicular ($x$ axis) to the far-Þeld director $\mathbf{n}_0$ for CPN oriented in the plane ($x$ axis) (c) and out of the plane (between $z$ and $x$ axes) (d) of a planar cell; insets show dark-Þeld textures of corresponding CPNs. The size of insets is $8 \times 8$ μm$^2$. Solid lines are a Þt with Eq. (1) (e) Histograms of angular displacements of CPN around $\mathbf{n}_0$ collected for  10 min in a homeotropic cell (

at both ends [26,29]. In dark-field microscopy observations, CSNs appear as bright elongated spots that, on average, align along $n_0$ to minimize the free energy due to particle-induced elastic distortions and surface energy of anisotropic molecular interactions at particle surfaces. The anisotropy of translational diffusion of CSNs is large ($D_{||}/D_{\perp} > 2$) (Table I

FIG. 3. (Color online) Diffusion of NBN nanoparticle in a nematic liquid crystal. (a) Schematic diagram of NBN and surrounding director Þeld $n(r)$ (thin blue lines). (b) Mean square displacements along

anisotropy from $D_a/D_b < 1$ to $D_a/D_b > 2$ as compared to what is expected for particles with similar shapes dispersed in isotropic hosts (see the example of NBNs in LC and oblate spheroids in isotropic fluids compared in the Table I). The rotational diffusion is also anisotropic and depends on the orientation of the rotation axis with respect to $n_0$ [compare Figs. 1(e) and 2(c)–2(e)]; it is faster around $n_0$ [Figs. 1(a) and 1(e)]. The rotational diffusion around the axis normal to $n_0$ is strongly hindered or bound by the LC elasticity [Figs. 2(a) and 2(e)]. Often, as in the example of CPNs, the anisotropy of translational diffusion is coupled to the rotational diffusion [Figs. 1(c) and 1(d)]. Furthermore, translational self-diffusion of nanorods can be significantly altered *in situ* using the capping with photosensitive and mesogenic ligands (Fig. 5).

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