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Synchronized oscillations of dimers in biphasic charged fd-virus suspensions

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Micron-sized colloidal spheres that are dispersed in an isotropic-nematic biphasic host suspension of charged rods (fd-virus particles) are shown to spontaneously form dimers, which exhibit a synchronized oscillatory motion. Dimer formation is not observed in the monophase of isotropic and nematic suspensions. The synchronized oscillations of dimers are connected to the inhomogeneous state of the host suspension of charged rods (fd viruses) where nematic domains are in coexistence with isotropic regions. The synchronization of oscillations occurs in bulk states, in the absence of an external field. With a low field strength of an applied electric field, the synchronization is rather reduced, but it recovers again when the field is turned off. In this Rapid Communication, we report this observation as an example of the strange attractor, occurring in the mixture of PS (polystyrene) dimers in an isotropic-nematic coexistence biphasic fd-virus network. Furthermore, we highlight that the synchronization of PS-dimer oscillations is the result of a global bifurcation diagram, driven by a delicate balance between the short-attractive "twisted" interaction of PS dimers and long-ranged electrostatic repulsive interactions of charged fd rods. The interest is then in the local enhancement of "twist-nematic" elasticity in reorientation of the dimer oscillations. An analysis of image-time correlations is provided with the data movies and Fourier transforms of averaged orientations for the synchronized oscillations of dimers in the biphasic I-N coexistence concentration of charged fd-virus suspensions.

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When a system exhibits two minima in its free energy as a function of a given order parameter with similar depths, which are separated by a small energy barrier of at most a few times the thermal energy, it will persistently switch between the two corresponding states. In a multidimensional order-parameter space, the existence of two free-energy minima may result in a so-called strange attractor where the system switches between the free-energy minima through quasistochastic orbits in the order-parameter space [1]. A biological example that exhibits this behavior is the dimer oscillation in Hes-Her dimer proteins of zebrafish, where synchronized segmental oscillations serve as a clock [2]. In this Rapid Communication, we describe a similar behavior observed in a dispersion of colloidal spheres in a host suspension of charged colloidal rods in the isotropic-nematic biphasic concentration. The spontaneous formation of polystyrene (PS) dimers occurs on dispersing single PS spheres in an isotropic-nematic biphasic phase of charged fd-virus particles, and surprisingly, synchronized oscillation appears with reorientation of the dimer oscillations. However, the spontaneous formation of dimers is not observed in the monophase of isotropic or nematic suspensions of fd-virus particles. Domain boundaries thus play an essential role in the spontaneous formation of PS dimers. A possible mechanism for the formation of dimers and the observed synchronization of PS-dimer oscillations is possibly due to the above mentioned existence of two free-energy minima for a dimer as a function of the distance between the two spheres within the dimer, as mediated through the interaction of two spheres within the nematic domain boundaries. The degree of synchronization is observed to be reduced upon applying a weak electric field, which has little effect on single PS-sphere dynamics. The synchronized motion is fully recovered by switching off the electric field.

The PS microspheres are prepared by dispersion polymerization of purified styrene monomer, with polyvinylpyrrolidone (molecular weight $M_w \sim 55$ Kg/mol), 2-azobisisobutyronitrile, and ethanol used as a stabilizer, initiator, and dispersion medium, respectively [3]. The inset of Fig. 1(a) shows a scanning electron micrograph of the PS spheres, which have a diameter of 1.5 μm. The negatively charged PS spheres in powder form are dispersed in a low ionic strength (0.032 mM) Tris-HCl buffer. Dynamic light scattering correlation functions on dilute dispersions of PS spheres (without the fd-virus particles) are shown in Fig. 1(a), both in the absence and presence of an external electric field. Here, the wavelength of the He-Ne laser light is 633 nm (JDS Uniphase Model 1145P), and an ALV-5000/EPP multiple tau digital real time correlator is used. The scattering angle corresponds to a length scale of 2.7 μm, so that displacements of the PS spheres are probed over distances that are comparable to their own size [4]. The peak in these correlation functions is due to heterodyning. As can be seen from these correlation functions, the typical weak electric-field strengths that we apply in the present study (less than 3 V/mm) have no significant effect on the dynamics of single PS spheres. The effect of electric fields on the dynamics of PS spheres at much higher field strengths has been studied before as electrorheological fluids, where dielectric polarization is important [5]. In the presence of such high field strengths (typically larger than 100 V/mm), dielectric polarization of the interface between the particles and the solvent leads to PS-sphere interparticle interactions which give rise to the formation of strings. However, for the weak fields applied in the present study, there is no significant effect on the behavior of the PS-sphere dispersions.

Also, for the host system of charged rods in which the PS spheres are embedded, suspensions of fd-virus particles are used. Fd-virus particles are highly charged (a total charge of 10 000 elementary charges), consisting of a helical DNA strand, covered with about 2700 coat proteins [6]. The length

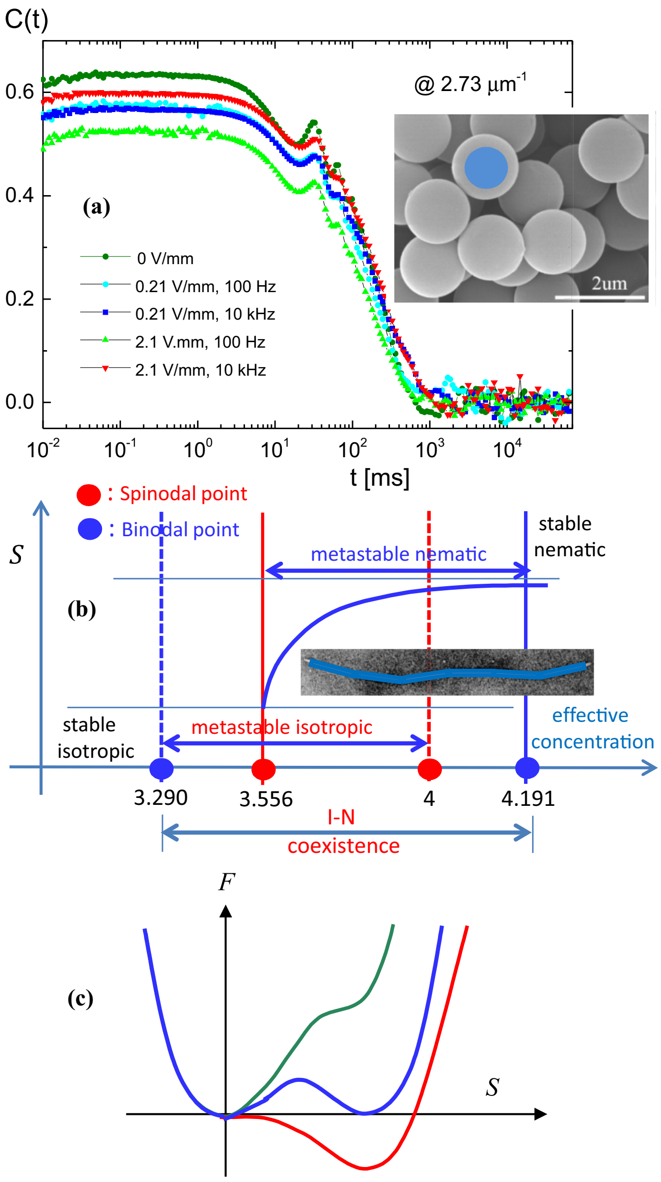

FIG. 1. (a) *In situ* electric-field dynamic light scattering of polymerized PS spheres in a low ionic strength of Tris-HCl buffer solution (0.032 mM), for various field conditions at a fixed scattering wave vector. The inset is the scanning electron micrograph of the PS sphere. (b) A brief sketch of an order parameter versus concentration phase diagram of the host system of colloidal rods (of fd viruses), where two spinodal and binodal points are indicated with the isotropic-nematic (I-N) coexistence concentration. (c) Corresponding free-energy function as a function of the order parameter for rod suspensions: I-N biphasic state (blue line) is under instability between lower (green line) and upper (red line) binodal concentrations.

of a fd-virus particle is 880 nm, and the core thickness is 6.8 nm, with the persistence length of 2200–2500 nm [see the inset of Fig. 1(b)]. The ionic strength in the present experiments is very low, 0.032 mM, corresponding to a relatively large Debye screening length of 54 nm [7]. At this low ionic strength, the effective diameter that measures the range of electrostatic interactions is a few times larger than the bare core diameter [8]. For lowering the ionic strength of the suspension of a highly charged fd virus, different phase, longer electrostatic interactions are exhibited in the phase behaviors [9]. At the very low ionic strength used here, the isotropic-nematic phase boundaries are located at relatively quite low fd concentrations [7], while no sedimentation occurs of nematic domains in the biphasic region over a time span of many hours. PS is used as a tracer method, meaning that it is very diluted as compared to the suspensions of the fd virus so that the PS is expected to not interact, itself, in the medium of fd-virus networks. Thus the phase diagram of the fd virus should not be influenced by the presence of PS particles. This is the reason that the Brownian motion of PS is seen not only in an isotropic, but also in a nematic fd-virus network.

The structure and dynamical correlations of diluted suspensions of charged fd-virus rods have been studied before by Monte Carlo simulations [10] and Brownian dynamics simulation [11], as well as the dynamics of isotropic-nematic and shear-induced I-N transition [12], and the stabilization of the chaotic state under shear stress [13]. However, as far as we know, there is yet no direct observation that experimentally found dimer oscillations in the bifurcation diagram of an I-N coexistence concentration, as resulting in the formation of a strange attractor. Figure 1(b) is a brief sketch of an order parameter versus a concentration phase diagram of colloidal rods (of fd viruses), where two spinodal and binodal points are indicated with the I-N coexistence concentration. Here the effective concentration is estimated by Onsager's theory [8], independent of ionic strength. The resulting long-ranged electrostatic interactions lead to an effective potential trap such that each particle is within the energy landscape set by neighboring particles. For elongated particles, a nonlinear self-consistent Smoluchowski equation for orientational distributions can be described by the Maier-Saupe model, where nonequilibrium free energy and entropy are estimated for the time evolution of an order parameter [14]. Free energy is shown as a function of the order parameter in Fig. 1(c), which now indicates the global minimum is corresponding to the I-N bistable state order parameter. Such slightly perturbed free-energy function is shown for lower binodal and upper binodal concentrations in Fig. 1(c). The effect of a high electric field on the suspension of polystyrene alone is reported by a dynamic light scattering such that the decay rates are proportional to the viscosity changes in the presence of an electric field [5]. PS is one of the candidates for electrorheological fluid, where the dispersion consists of uniform dielectric spheres. In the presence of an electric field, polarization occurs at the interface between the particles and the solvent. Dilute suspensions of permanent electric dipole moments and electric polarizability to an applied electric field are also shown with nonlinear relaxation of time-dependent polarizability, and the optical susceptibility. However, at a low electric field strength, there are no significant differences in the intensity-autocorrelation functions [see Fig. 1(a)], as compared to the absence of an external electric field. The oscillation of a small scattering amplitude appears at roughly the time window of 35–40 ms, which is a similar range of relaxation time to that of the host system of the charged fd virus for an isotropic-nematic coexistence concentration [4].

In the absence of an external electric field, the morphologies of the mixture of charged PS spheres in the isotropic,

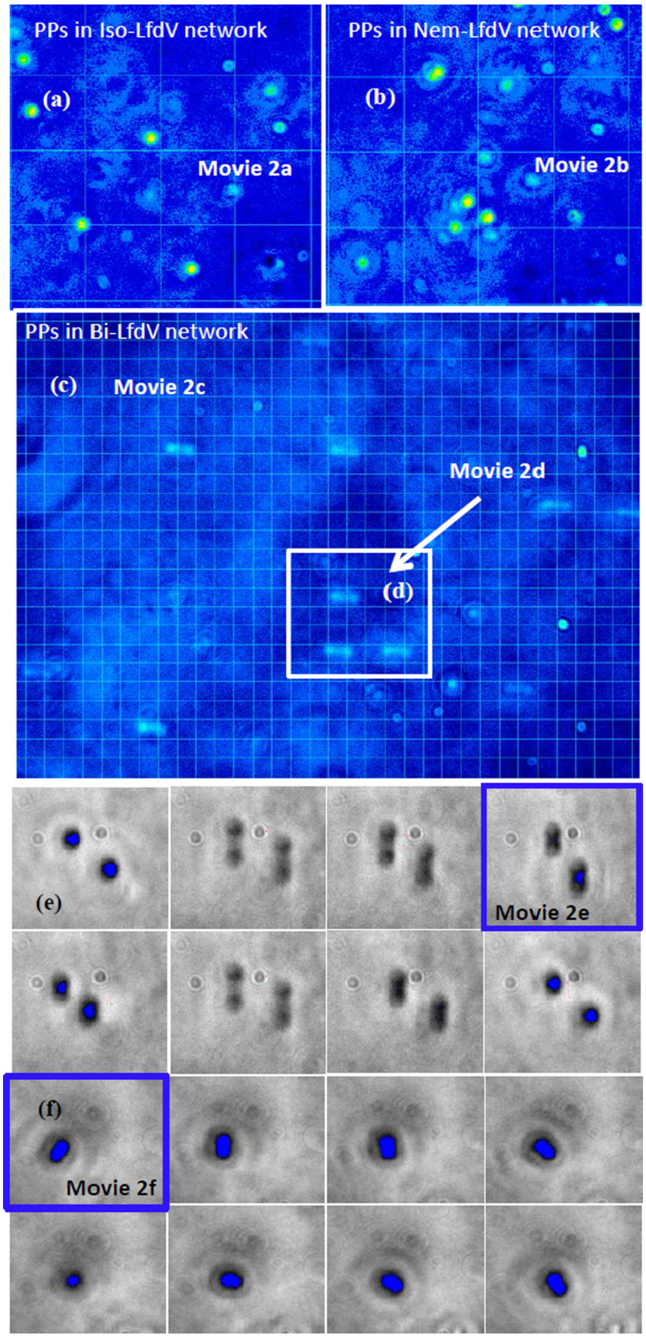

FIG. 2. Optical morphology and movie data for Brownian motion of polymerized PS spheres in a monophase of (a) an isotropic fd-virus network, and (b) in a nematic fd-virus network. (c) and (d) show the synchronization of PS-dimer oscillations in an I-N coexistent biphasic fd-virus network. (e) A few temporal snapshots of different orientations of dimer oscillations in the bulk state, and (f) the rotations of dimers without oscillations in thin cell thickness. Blue is coded for the lower part of the image, and the time step is 0.25 s. Supplemental Material movies (movies 2a, 2b, 2c, 2d, 2e, and 2f) are provided.

nematic, and I-N coexistence biphasic rod networks (for a fd concentration of 1.0 mg/ml) are shown with the optical morphology and corresponding movie data (movie 2a, movie 2b, movie 2c [15]) in Figs. 2(a), 2(b), and 2(c), respectively. First of all, Brownian motions of single PS spheres (of 1.5 μm diameter) are observed in the monophase of the host system, in either an isotropic [Fig. 2(a)] or the nematic fd-rod network [Fig. 2(b)]. However, for an I-N biphasic host of fd-rod network [Fig. 2(c)], not only dimers of PS spheres are formed with oscillations, but also vivid motions of synchronized dimer oscillations appear, whose visualization can be seen in movies 2c and 2d, as the distance between two PSs in the dimer is oscillating, and this oscillation is synchronized for all the dimers in the solution. The synchronization of PS-dimer oscillations occurs only in a bulk state (with the cell thickness of 1.0 mm). The direct visualization of a few snapshots of different bulk reorientations of two neighboring PS dimers in the biphasic fd-virus networks are provided in Fig. 2(e).

For lowering the sample thickness (of a 0.5-mm-thick cell) in the same biphasic host concentration, dimer oscillations are not seen, but only free rotations of “tightly” packed dimers are detected, consisting of two attached PS spheres, without a separation, in Fig. 2(f). This confirms that the existence of dimer oscillations is related to the bulk isotropic-nematic domains, as a global bifurcation process. The transient reorientations of PS-dimer oscillations of biphasic fd-rod networks are presented in Figs. 3(a)–3(c), with their morphological snapshots, on the right side, in which those orientations occur instantaneously in a bulk state. A reason for the formation of PS dimers in the biphasic fd-rod network is that the spatial coherence length of charged fd-virus suspensions is found to be the minimum length scale at an isotropic-nematic coexistence concentration. This may indicate that a “local” enhancement of “twist”-nematic elasticity will play a role in the $N*$-phase, which is briefly sketched in the middle of Fig. 3(d). The anisotropic deformation of the director field is depicted as the I-N biphasic fd-rod network, and related to the “strange attractor” of the biphasic rod network (of Iso + Nem). Thus the strange attractor is shown as a torus-tube shape, not the butterfly shape that can be related to the latter cases of lower and upper binodal concentration. Also, at a higher field amplitude, sudden changes of the flux of PS dimers are seen in a periodic manner (of larger times of a few tens of seconds) with the reversed flow due to the electric polarization at a low salinity [16].

The quantification of kinetics of dimer oscillations is then performed by an image-time correlation function [4], obtained from the collection of time-lapsed images, as follows: Let $I(t)$ be the instantaneous transmitted intensity detected by a given pixel of the CCD camera (AxioCam Color A12-312 CCD camera, with a chip of 1300×1030 pixels). From time traces recorded for all these pixels, the image correlation function $C_V(t)$ is computed, which is defined as

$$C_V(t) = \frac{\langle [I(t) - \langle I(t)\rangle]\,[I(0) - \langle I(0)\rangle]\rangle}{\langle [I(0) - \langle I(0)\rangle]^2\rangle}, \qquad (1)$$

where the brackets $\langle \cdots \rangle$ denote averaging over all CCD-camera pixels. Each single image in a time trace is used to construct an image correlation function from the region of interest as 300×300 pixels. The above definition of the image-time correlation function is reminiscent of the intensity correlation function as obtained from dynamic light scattering, except that the intensity here is not a scattered intensity but the transmitted intensity through the two crossed polarizers. Details of image-time correlation spectroscopy can be found in

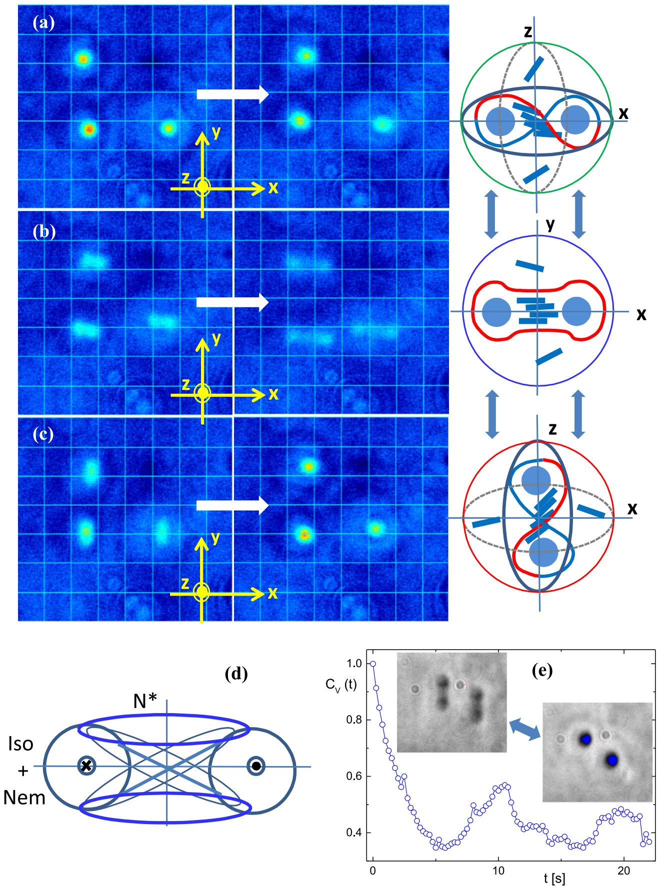

FIG. 3. (a)–(c) A few snapshots and possible schemes of synchronized dimer oscillations: (a) Dimers formed in the absence of an external field, but soon oscillate to a planar state in the x-y direction in the right panel. (b) Fully stretched in the x-y plane, and (c) local orientation changes to the z axis, before it returns to the state (a). (d) A brief sketch of the strange attractor, where the local twist-nematic, N^* phase may exist between dimer oscillations, within nematic domains in an isotropic background. (e) An image-time correlation function obtained from the movie data of movie 2e, with two distinguishable configurations of dimer orientations.

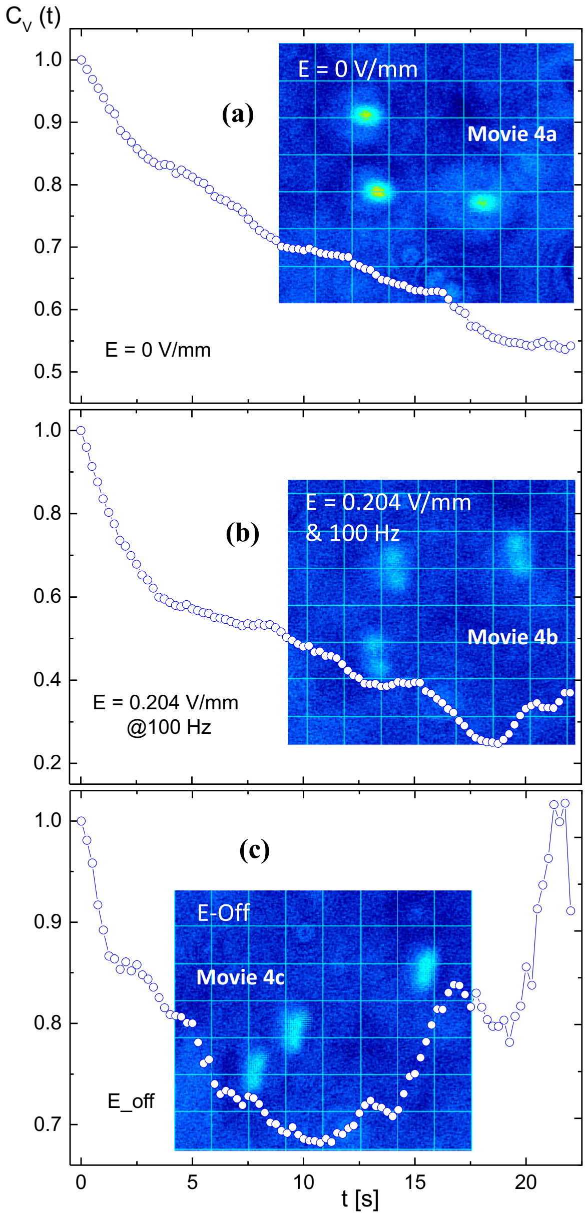

FIG. 4. Image-time correlation functions and the movie data, performed in different electric-field conditions: (a) 0 V/mm, (b) 0.204 V/mm and 100 Hz, and (c) turning off the electric field. Supplemental Material movies (movies 4a, 4b, and 4c) are provided.

Ref. [4]. Two particular distinguishable configurations of PS-dimer oscillation are shown in Fig. 3(e), with an image-time correlation function obtained from the time-lapsed images of the movie data of movie 2e: one is the fully stretched in planar orientation, and the other is "reoriented" towards vertical (as "stand-up") orientation. Further analyses on the image-time correlations for different electric-field conditions are also shown, with corresponding movie data in Fig. 4: In the absence of an electric field, a rather slow decay rate of different steps of dimer oscillation appears in Fig. 4(a); however, as soon as a low electric field is applied, in Fig. 4(b), a fast decay occurs immediately and progresses further to a lower value for different states of synchronized dimer oscillations. The intriguing fact is that, when the external electric field is turned off, the image-time correlation functions are increased again [Fig. 4(c)]. This means that the PS-dimer oscillations in a biphasic fd-rod network are fundamentally determined by the stability of a coexistence concentration, set by a thermodynamic equilibrium, and the synchronization occurs in the collective motions of the I-N biphasic phase.

A further check on the reorientation of synchronization of these dimer oscillations is done using Fourier-space images that are generated in time [Figs. 5(a) and 5(b)], for a larger field of views [see the dimension of Fig. 2(c)]. Typical Fourier-transformed (FT) images are shown in Fig. 5(c), for turning off the field; both the four-edged circles and the center indicate reorientations of PS dimers themselves in a biphasic host of fd-rod network. Here, note that the center of the FT images not only contains anisotropic distributions, but it also reorients locally in time, as depicted in the separate view of movie 5d in Fig. 5(c). A few snapshots of the FT image of the

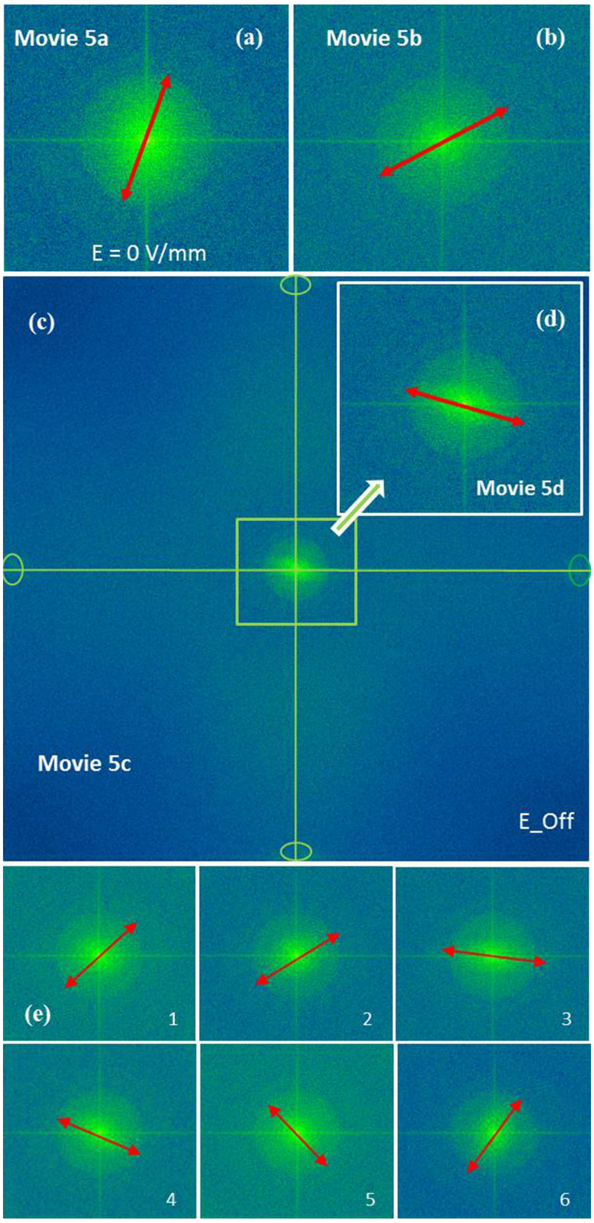

FIG. 5. Fourier transforms of different electric-field conditions: (a) 0 V/mm, (b) 0.204 V/mm and 100 Hz, and (c),(d) turning off the electric field. (e) A few snapshots of different orientations for turning off the field, with a time step of 0.5 s. The red arrow indicates the average axis of an orientation. Supplemental Material movies (movies 5a, 5b, 5c, and 5d) are provided.

center [Figs. 5(c) and 5(d)] are provided in Fig. 5(e). Similar features exist in both the absence and the presence of an electric field, in Figs. 5(a) and 5(b), respectively.

A brief summary of the synchronized oscillations of PS dimers in biphasic charged fd rods is as follows: (i) Here the strange attractor is visualized in a mixture of PS spheres in the host of isotropic-nematic coexistent biphasic charged fd-rod networks, not in the monophase of isotropic (and nematic) phase. The PS spheres are bounded with the charged fd rods effectively such that two initially different states of order parameter are needed to form the stable PS dimers. (ii) With a weak perturbation of an external electric field, the synchronization of dimer oscillations seems to be somewhat constrained, but not much affected by low electric fields, only reduced to a moderate separation distance. (iii) When the field is turned off, the synchronization recovers again, mimicking the equilibrium state of dimer oscillations. Thus the synchronization is driven by a complete global state of "blurry" nematic domains in an isotropic background, which is similar to the nature of the field-induced dynamic states [17], where "transient" order parameter kinetics vary in local space and time in the I-N coexistence concentration. (iv) The synchronization is further visualized by Fourier transforms of dimer oscillations, showing coexistence orientations of isotropic and anisotropic distributions in a larger field of views in Fig. 5. Since there is no formation of dimers in the monophase of an isotropic and nematic network, the synchronized PS-dimer oscillations are purely the result of an energy barrier that is bounded by the effective interaction of PS dimers in the neighbors of isotropic-nematic coexistence charged fd-rod networks.

Therefore, it is quite an intriguing demonstration to show the local short-ranged attraction of two charged PS spheres forming a dimer with oscillations, which is assisted by the twist elasticity of charged fd rods between PS dimers. The synchronization is then controlled by the globally repulsive nature of electrostatic interactions in the isotropic-nematic biphasic network of charged fd viruses. The short-ranged attraction of PS dimers is then the consequence of the minimized free-energy barrier in the I-N biphasic concentration, and less by direct interaction of PS spheres and fd rods. We hope this observation is useful to provide some aspect of effective electrostatic interactions of a charged complex system of spheres in the host of I-N biphasic rod networks, and furthermore to design novel microscopic motors in demixing complex fluids.

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