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Dynamics of ordered colloidal particle monolayers at nematic liquid crystal interfaces[†]

Wei-Shao Wei,*^a Mohamed Amine Gharbi,^{bc} Matthew A. Lohr,^a Tim Still,^a Matthew D. Gratale,^a T. C. Lubensky,^a Kathleen J. Stebe^d and A. G. Yodh^a

We prepare two-dimensional crystalline packings of colloidal particles on surfaces of the nematic liquid crystal (NLC) 5CB, and we investigate the diffusion and vibrational phonon modes of these particles using video microscopy. Short-time particle diffusion at the air–NLC interface is well described by a Stokes–Einstein model with viscosity similar to that of 5CB. Crystal phonon modes, measured by particle displacement covariance techniques, are demonstrated to depend on the elastic constants of 5CB through interparticle forces produced by LC defects that extend from the interface into the underlying bulk material. The displacement correlations permit characterization of transverse and longitudinal sound velocities of the crystal packings, as well as the particle interactions produced by the LC defects. All behaviors are studied in the nematic phase as a function of increasing temperature up to the nematic–isotropic transition.

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1 Introduction

Colloidal particles at traditional liquid interfaces are known to form ordered and disordered structures driven by electrostatic,^{1–5} magnetic,^{6–8} and capillary forces.^{9–12} Particles at liquid crystal (LC) interfaces, by contrast, exhibit self-assembly driven by elastic interactions that arise in the underlying anisotropic fluid.^{13–18} For example, micron-sized colloidal particles form patterns ranging from hexagonal lattices to chain-like dipole structures at water–LC interfaces^{14,15} and air–LC interfaces.^{16,17,19} Previous studies of these systems have investigated effects of anchoring conditions and geometry on structure formation. The dynamics associated with these structures, however, remains largely unexplored. Moreover, though LC-induced particle potentials have been studied with optical tweezers in simple two-particle systems,¹⁶ the interparticle interactions characteristic of manyparticle systems have not been measured.

In this contribution we explore dynamics and packings of colloidal particles confined to the interface bounded on one side by air and on the other side by the thermotropic nematic liquid crystal (NLC) 4-cyano-4'-pentylbiphenyl (5CB). The resulting ensemble of colloidal particles differs qualitatively from other classic two-dimensional (2D) systems^{1-4,7,8} in that the interparticle

^d Department of Chemical and Biomolecular Engineering,

forces are mediated *via* liquid crystalline defects which extend from under each particle into the bulk LC, *i.e.*, into the underlying semi-infinite medium. Thus, the experimental system offers a unique sample for study of 2D phase transitions, for study of exotic particle dynamics, and for study of crystal phonons and LC defect interactions in a regime wherein many-body effects can be important.

Here we employ video microscopy and particle tracking to measure short-time particle diffusion and vibrational phonon modes of the 2D crystals at the air-NLC interface. The full phonon density of states of the ordered lattice at the interface exhibits Debye behavior at low frequencies and van Hove-like singularities at higher frequencies. Sound velocities are readily extracted from the phonon dispersion relations, and interparticle interactions in the crystals are derived from the covariance matrix of particle displacements. All of these parameters are investigated as a function of temperature up to the nematic-isotropic LC transition. The variation of the resulting Brownian dynamics and potentials are consistent with the measured temperature dependence of 5CB elastic constants and viscosity.²⁰⁻³⁰ Finally, qualitative observations of structural melting are reported. Information thus gained takes valuable steps towards using this class of particle/air-NLC interface to probe phase behavior phenomenology of quasi-2D materials and to probe properties of the underlying LC.

2 Experimental section

The particle monolayer was made by trapping dry micron-sized silica particles at the interface between air and the bulk nematic phase 5CB following schemes described in ref. 16. Briefly,

^a Department of Physics and Astronomy, University of Pennsylvania, Philadelphia, Pennsylvania, 19104, USA. E-mail: weiwe@sas.upenn.edu; Tel: +1 (215) 573-7775

^b Department of Physics, McGill University, Montreal, Quebec, Canada

^c Department of Chemistry, McGill University, Montreal, Quebec, Canada

University of Pennsylvania, Philadelphia, Pennsylvania, 19104, USA

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Paper

circular-shaped wells (\approx 1.5 cm in diameter) were fabricated by mounting a spacer with thickness of 100 µm onto a glass slide. The wells were then filled with the LC 5CB (Kingston Chemicals). Silica microparticles (nominal diameter d = 1.0 µm, Duke Standards) were surface-functionalized with dimethyloctadecyl [3-(trimethoxysilyl)propyl] ammonium chloride (DMOAP, Sigma-Aldrich; 5 wt% in a 1:9 by weight mixture of water and ethanol). This functionalization induces homeotropic anchoring of 5CB LC mesogens on the particle surfaces. After being aerosolized by an air pulse, the particles settled through the air and were adsorbed on the air-exposed surface of 5CB [see Fig. 1(a)]. The bottom glass slide was also treated with a 5 wt% DMOAP solution for homeotropic anchoring.

The whole system was heated to the nematic-isotropic transition temperature, $T_{\rm NI} \approx 35$ °C, for a short time and then cooled before the colloidal particles were spread. This heating-cooling scheme provides an opportunity for the LC mesogens to rearrange and helps to ensure uniform director alignment in the vertical direction within the bulk LC, *i.e.*, before particles are introduced. In total, these cautionary measures help to minimize alignment complications caused by the bottom well surface and by disorder that can arise during sample loading

[*i.e.*, the procedures help to ensure uniform homeotropic alignment of the 5CB film as sketched in Fig. 1(a)]. Moreover, since the thickness of NLC film ($\approx 50 \ \mu$ m) is much larger than the colloidal particle diameter, the system dynamics are barely sensitive to the NLC film thickness and the analyses of the problem is simplified. A glass coverslip was also added over the well to minimize air flow effects.

After the microparticles settle at the air–NLC interface, defects form to satisfy anchoring conditions on the particle surface and at the air–NLC interface.³¹ One possible director configuration [shown in Fig. 1(b) and (c)] is produced by a point defect beneath each particle. Macroscopic ordered patterns of such particles spontaneously form after the samples stabilize over a few days. This particle self-assembly arises from an interplay between long-range LC-mediated interparticle elastic repulsion and a very weak gravitational confinement induced by the curved interface near the well edge. The weak gravitational confinement, in particular, ensures that a large surface–particle density is maintained.

Our experiments focus primarily on properties of particles in the resulting 2D hexagonal crystal [see Fig. 1(d)], which typically occupies $\approx 20\%$ of the sample well area. Grain boundaries and



Fig. 1 (a) DMOAP functionalized silica colloids spread at the air-5CB interface. (b) The cartoon schematic depicts a possible local deformation of director alignment and a point hedgehog defect beneath each particle in the underlying LC. This cartoon is a faithful representation of the actual particle configuration, *i.e.*, with the majority of particles submerged. (c) Under cross-polarizers and in the top-view, four bright lobes around each particle exhibit the optical effects of the radial alignment of LC mesogens (below the surface). (d) Self-assembled hexagonal lattices form at large surface-particle density. Here the full-wave retardation plate is employed to distinguish northwest-southeast lobes (yellow/orange) and northeast-southwest lobes (blue), thereby further clarifying the local alignment of LC molecules. (e) Trajectories of a few colloidal particles within the whole field-of-view are shown. The scale bar represents 1 μ m, and all particles have a diameter of 1 μ m.



Fig. 2 As the temperature increases, the underlying LC 5CB undergoes a phase transition from (a) an orientationally ordered nematic phase (temperature below T_{NI}) to (b) a disordered isotropic phase (temperature above T_{NI}). The corresponding LC-mediated interparticle repulsive forces weaken and eventually vanish due to loss of mesogen alignment, and concurrently, (c) the crystalline hexagonal pattern of colloids begins to melt a few seconds after the phase transition temperature is reached. Particles have a diameter of 1 μ m.

defects sometimes arise too and thus further sub-divide the crystalline region into smaller "domains" with cross-sections of approximately several hundred micrometers. The temperature of the system is controlled by an indium tin oxide coated glass heating stage with mounted thermocouple. Most of the measurements were carried out at temperatures below $T_{\rm NI}$ of 5CB. When the LC undergoes a phase transition from the nematic to the isotropic phase, the aligned nature of LC mesogens vanishes, which in turn leads to the disappearance of defects. As a result, LC-mediated long-range interparticle repulsive forces disappear. This effect causes the crystalline hexagonal pattern to melt as shown in Fig. 2. Once the LC is in the isotropic phase, the colloidal particles experience unconstrained Brownian motion but eventually aggregate when particles come into close contact. This aggregation at very short range is possibly caused by weak capillary attractions between particles due to a very small deformation of the interface³² around isolated beads, but it could also be due to other more direct interactions or combinations thereof.

Sample images were acquired at 22 frames per second using dark-field video microscopy. Approximately 80 000 frames were utilized for most of the analyses. The only exception was the data set for the study of short-time particle diffusion; in that case, data was taken more rapidly, *i.e.*, at 110 frames per second with \approx 2000 frames in total. Higher frame rates are needed to resolve short-time diffusive behavior. Approximately 750 particles are contained within the field-of-view, *i.e.*, the region wherein data were acquired, which corresponds to approximately 2250 nearest-neighbor particle pairs. Trajectories of colloidal particles in the field-of-view were obtained *via* standard particle tracking techniques;³³ a typical particle trajectory is shown in Fig. 1(e).

We employed the displacement covariance matrix method^{34–38} to derive vibrational (phonon) properties of our dense particle packing. Briefly, we extracted displacement vectors, u(t), from the track file. This vector contains the displacement components of each particle in each frame (*i.e.*, at each timepoint, *t*), measured with respect to its equilibrium (steady-state) position. The time-averaged displacement covariance matrix, *C*, was calculated as follows:

$$C_{ij} = \langle u_i(t)u_j(t) \rangle_t, \tag{1}$$

where *i*, *j* denote particle numbers as well as coordinate components (*i.e.*, *x* and *y* directions in 2D). In the harmonic approximation, the stiffness matrix κ is related to *C* by

$$\kappa_{ij} = k_{\rm B} T(C^{-1})_{ij},\tag{2}$$

where $k_{\rm B}$ is the Boltzmann constant and *T* represents the temperature. Its elements κ_{ij} give the effective spring constants between particles *i* and *j*, including both *x*- and *y*-components. In the past,^{34–38} this analysis has been employed for isolated systems. However, for lattice structure with boundary confinements (*e.g.* our case), the effect of stress in the system must also be considered.^{39,40} In this case, the *x*- and *y*-components for each particle pair α , β are extracted from the elements κ_{ij} using a 2 2 submatrix:

$$\bar{\kappa}_{\alpha\beta} = \left[\begin{pmatrix} \kappa^{xx}_{\alpha\beta} & \kappa^{xy}_{\alpha\beta} \\ \\ \kappa^{yx}_{\alpha\beta} & \kappa^{yy}_{\alpha\beta} \end{pmatrix} \right] \left[\begin{pmatrix} & (3) \end{pmatrix} \right]$$

Diagonalizing $\bar{\kappa}_{\alpha\beta}$ gives two sets of eigenvalues and eigenvectors; one set is directed along the bond *b* between particle pair (denoted as κ_{eff}) while the other set has direction perpendicular to the bond (denoted as σ_t/r). The former (parallel) eigenvalue is the effective spring constant for this specific colloidal particle pair, and the latter (perpendicular) eigenvalue is related to the stress divided by the center-to-center separation of the two interacting particles, *r*.

Finally, we obtain the dynamical matrix, D_{ij} , of the system from

$$D_{ij} = \underbrace{\kappa_{ij}}{m}, \tag{4}$$

where *m* is the particle mass. Diagonalization of D_{ij} gives the eigenvalues and eigenvectors of the vibrational phonons of the system. (Note, the system characterized by this procedure is the so-called shadow particle system with the same interactions and geometry as the experimental system, but absent damping.) We encourage the interested reader to consult ref. 34–38 for details about the method, including its strengths and limitations.^{41–44} To our knowledge, the present analysis is the first to incorporate the effects of confinement stresses. The eigenvalues of the dynamical matrix are the square of the eigenfrequencies, ω , of the phonon modes, and the eigenvectors indicate the

displacement amplitude for each particle associated with each mode. The accumulated number of modes, $N(\omega)$, is defined as the number of vibrational modes with frequency less than or equal to ω , and the derivative of $N(\omega)$ with respect to ω is the phonon density of states (DOS), *i.e.*, the number of vibrational modes per unit frequency (energy) interval.

In carrying out this covariance procedure, caution must be taken because several factors can introduce errors. All of these procedures have been carefully described by Chen *et al.*⁴⁵ Notably, we use a linear extrapolation method³⁸ to account for the effects of finite sampling on the mode frequencies.

3 Results and discussion

3.1 Short-time particle diffusion

We first report on diffusion dynamics. We calculated the particle mean square displacement (MSD) from the individual trajectories as shown in Fig. 3(a). The plateau at long time delays is caused by spatial caging of particle motion due to its local hexagonal confinement cage in the ordered structure. At the early times we expect the MSD to grow linearly with time, and, indeed, the particles at the air–NLC interface exhibit fairly linear short-time MSD curves. We varied temperature, and we fit the short-time MSD at each temperature to derive temperature-dependent Brownian dynamics [Fig. 3(b)]. The linear fits gave the short-time diffusion coefficient, \mathfrak{D} , as a function of temperature [Fig. 3(c)]. The observation that \mathfrak{D} increases with temperature is sensible; higher temperature implies weaker elastic forces and viscosity and thus faster diffusion. To quantitatively explain this tendency, we apply a very simple model that assumes particle diffusion at the interface is dominated by the bulk LC. In this case, the diffusion coefficient is described by the Stokes–Einstein relation,⁴⁶

$$\mathfrak{D} = \underbrace{\frac{k_{\mathrm{B}}T}{6\pi R\eta}},\tag{5}$$

where η is the viscosity of 5CB, and *R* is the colloidal particle radius. Generally, for diffusion in a LC, the anisotropic nature of the viscosity should be considered,^{47–49} and an anisotropic drag force is predicted.^{50–52} However, the particle motions in the present situation are largely in-plane, and therefore we need only consider the viscosity η_1 for which the LC director is perpendicular to the direction of particle motion and parallel to the direction of velocity gradient. This approach, while approximate, is sensible because the particle motions are restricted in 2D by the air–NLC interface.



Fig. 3 (a) The mean square displacement (MSD) is calculated from colloidal particle trajectories. At short times, diffusive behavior is observed (MSD grows linearly with time; the grey solid line has slope = 1). The plateau at long time intervals is caused by lattice caging effects. (b) The linear fit of the short-time MSD at each temperature gives (c) a corresponding short-time diffusion coefficient, \mathfrak{D} , as a function of temperature (blue dots with error bars); \mathfrak{D} increases with increasing temperature. The dark-red dashed curve shows T/η_1 as a function of temperature from previous work.²⁵ (d) A linear correlation between \mathfrak{D} and T/η_1 is exhibited over most of the temperature range probed, confirming a Stokes–Einstein model; deviation from linearity is evident when the temperature approaches the nematic–isotropic transition.

As a further check we note that because colloidal particles do not distort the shape of LC interface significantly, the Young equation should still provide guidance for the behavior of the anisotropic liquid.³² (Note, although the NLC with homeotropic anchoring yields a modified Young equation,⁵³ the air-5CB interfacial energy is large enough to justify neglect of the modified term.) In this case, the vertical position of colloids is controlled by the contact angle between silica particle and the air-5CB interface. Taking account the balance between tension forces at the three-phase contact line (particle-air, particle-LC, and air-LC interface), and including the effects of gravity and buoyancy, a simple geometric calculation gives a contact angle \approx 33 degrees, which agrees well with experimental measurements via surface profiler.³² This contact angle implies that more than 90% of the particle volume is immersed in 5CB. For these reasons, it is plausible that a single LC viscosity could dominate the drag force [*i.e.*, eqn (5) should capture most of the diffusion physics] for the particles. For comparison, we also show the dark-red dashed curve in Fig. 3(c), T/η_1 , plotted as a function of temperature;²⁵ it follows roughly the same trend as our experimental diffusion coefficient data (blue dots with error bars).

Assuming a linear correlation between \mathfrak{D} and T/η_1 , the linear fit gives $R \approx 0.54 \,\mu\text{m}$ as shown in Fig. 3(d), a value close to the actual particle size $R = 0.5 \mu m$. Note, here we have taken one value of η_1 for our calculation²⁵ while the measured viscosity values of 5CB vary somewhat across all previous work.²⁴⁻³⁰ Of course, different η_1 's will give slightly different fitted *R*'s. Further, we observed a deviation from linearity when the temperature approaches the nematic-isotropic transition. This deviation can be explained by a larger hydrodynamic radius experienced by the particle and caused by the comparatively stable surface-induced orientationally-ordered layer near the colloid-LC interface.⁵⁴ Alternatively, an effective viscosity arises as a result of different vertical positions of particles at the interface; this position variation could be induced by changing surface tension forces with increasing temperature, *i.e.*, effects that produce different weighting of the LC and air viscosities.

Thus, the short-time particle diffusion dynamics of our system are revealed to follow a bulk Stokes–Einstein relation with the temperature dependence of η_1 following that of bulk nematic 5CB. Ultimately, the air-exposed part of particle and interfacial effects should be considered for more precise analyses. For comparison, a single homeotropic anchored particle in its bulk nematic counterpart exhibits a slightly smaller diffusion coefficient than our experimental measurement at the air–NLC interface, possibly due to a larger effective viscosity. The difference is within 20%.^{51,52} Note also, the 3D Stokes–Einstein model is an approximation, and, ideally, it should be modified with a correction factor that accounts for the interface.⁵⁵

3.2 Phonon density of states and dispersion relations

As noted above, the phonon modes of the collective system with hexagonal order were calculated from the colloids' displacement correlations.^{34–38} From this data we derive the phonon

density of states (DOS) as a function of frequency ω . According to Debye model, the DOS of a crystal should scale as ω^{n-1} at low frequencies, where *n* is the dimension of the system.⁵⁶ Therefore, in the case of a 2D crystal, the DOS should grow linearly with the phonon frequency. The DOS of the 2D hexagonal lattice of particles at the air–NLC interface indeed follows the Debye model at low frequencies, as shown in Fig. 4(a).

In the higher frequency regimes, the DOS deviates from Debye scaling and displays two peaks that are remnants of van Hove singularities [Fig. 4(a)]. These features arise from transverse and longitudinal vibrational modes at the edge of the first Brillouin zone; they have been observed in other 2D colloidal crystal experiments with different interaction potentials.^{45,56,57}

Using the solutions of $D(\omega)$, we also calculated the phonon dispersion relation $\omega(q)$ for the system, where q represents the phonon wave vector. We extract $\omega(q)$ by Fourier decomposition



Fig. 4 (a) The vibrational density of states (DOS) of the hexagonal crystals of particles at the air–NLC interface is shown as a function of frequency ω . At low frequencies, the DOS grows approximately linearly with phonon frequency, *i.e.*, the Debye scaling DOS $\propto \omega$. In higher frequency regimes, the DOS deviates from Debye scaling and displays remnants of van Hove singularities. Inset: For the regime where $\omega < 1.5 ext{ 10}^4 ext{ rad s}^{-1}$, the data is re-plotted with both axes logarithmically scaled. The grey solid line has slope = 1, which is predicted by the Debye model. (b) Dispersion curves for transverse (red/orange) and longitudinal (black/grey) modes along high-symmetry directions, including raw data (crosses) and binned data (solid circles and squares with error bars). The DOS plot is shown again for easy comparison of frequencies. The measurement was performed at room temperature, 21.8 °C. Inset: High-symmetry directions in reciprocal space.

of eigenvectors along high-symmetry crystallographic directions. The details of the method are described in the literature^{58,59} and were recently applied to soft colloidal crystals⁴⁵ and glasses.⁶⁰ The phonon dispersion relation for our crystal is shown in Fig. 4(b). Slopes of the transverse and longitudinal branches in the long-wavelength limit near the center of the Brillouin zone give the transverse and longitudinal sound velocities, $c_T = 24.0 \quad 0.4 \text{ mm s}^{-1}$ and $c_L = 60.2 \quad 0.4 \text{ mm s}^{-1}$, respectively (see Fig. S1 in ESI† for fits). The group velocity for both branches becomes zero at the edges of the Brillouin zone, and the frequencies wherein these features are observed correspond to those of the van Hove singularities in Fig. 4(a).

With these sound velocities at hand, we are able to perform other self-consistency checks. For example, according to the Debye model, for a 2D system⁶¹

$$DOS(\omega) \equiv \frac{dN(\omega)}{d\omega} = \frac{L^2}{2\pi c^2} \quad \omega,$$
(6)

where L^2 is the area size of the system and c is the sound velocity. Eqn (6) assumes $c_{\rm T}$ and $c_{\rm L}$ are the same, but in practice they are often different. For both the transverse and longitudinal branches, substitution of the system size and the calculated 0.3) $10^{-8} \text{ s}^2 \text{ rad}^{-2}$ sound velocities gives a slope of (19.6 10^{-8} s² rad⁻², respectively, for the low 4.1) and (123.4 frequency linear dispersion in the corresponding DOS plots. Their sum can be tested against our experimental low frequency DOS curve [Fig. 4(a)]. Indeed, the calculated slope of $(143.0 \quad 4.1) \quad 10^{-8} \text{ s}^2 \text{ rad}^{-2}$ is close to the one obtained from the experimental fitting, $(183.6 \quad 1.5) \quad 10^{-8} \text{ s}^2 \text{ rad}^{-2}$, as shown by the dark-red dashed line. Small deviations may arise due to the anisotropic nature of the sound velocities within these crystals, but the data quality does not justify their consideration at this time.

We also explored the temperature dependence of the phonon behavior. A rough analysis shows that the range of eigenfrequencies becomes wider, and the distribution of effective spring constants broadens as the system temperature decreases (see Fig. S2 in ESI[†]). Some of these observations are sensible. The effective spring constant, for example, becomes larger with decreasing temperature due to an increase in magnitude of the elastic constants (see Section 3.4 for detail); this effect, in turn, should lead to an increase in the full frequency range of the DOS. Other possible sources of increased broadening include increased disorder induced by factors such as non-uniform particle wetting and slow relaxation of LC-particle contact lines⁶² especially at lower temperatures. The resultant heterogeneities could thereby contribute to the observed distribution broadening of effective spring constants and DOS. Moreover, the data also suggests that the system has a broader distribution of nearest-neighbor interparticle separations at lower temperatures, *i.e.*, even though the basic hexagonal symmetry of the lattice persists. Further, sound velocities in the crystal are observed to decrease with increasing system temperature. At higher temperature, a smaller effective spring constant (see Section 3.4 for detail) is consistent with a lattice containing weaker bonds between neighboring particles, which gives rise

to smaller sound velocities. These phenomena deserve more attention and will be explored in future experiments.

3.3 Interparticle interactions in the crystal

Line defects (disclinations) and point defects (hedgehogs) are singular regions within nematically ordered media. In the NLC bulk with homeotropic boundary conditions at two ends of planar cell, the director field is uniform. By analogy with electrostatics, the total topological charge in this case is zero. When a spherical particle with homeotropic anchoring is added into the system, a topological +1 charge is introduced and distortions of the uniform field arise to satisfy anchoring constraints on the particle surface. Since the director field in the cell is uniform at large distance, the nematic creates a defect of charge -1, *i.e.*, a point defect (hyperbolic hedgehog) or a line defect (Saturn ring) to compensate the particle's +1 charge.

The elastic interactions between particles in bulk LCs have been understood, calculated,⁶³ and checked by experiment.^{64–66} However, the situation for colloidal particles at air–NLC interfaces is more complex and less studied. In fact, the forces between particles at interfaces are still debated, with different studies describing and observing different interaction behaviors.^{13,14,16–18,67,68}

Our displacement covariance experiments provide measurements of $\kappa_{\text{eff}}(r)$ for the silica particles in the hexagonal lattice at the air-NLC interface [see eqn (2) and (3)]. Ideally, the form of the interparticle potential may be directly assessed from measurement of κ_{eff} as a function of r at fixed temperature. Further, since the temperature can be varied, the same procedure can be carried out repeatedly at different temperatures to explore effects of the temperature-dependent elastic coefficients of 5CB. From the covariance matrix method, the calculated $\kappa_{eff(ii)}$ are the spring constants between particles with different center-to-center separation and with boundary confinement. In principle, one can obtain information about interactions between first nearest neighbors, second nearest neighbors, etc. Here, due to signal-to-noise limitations, we focus only on adjacent particles, i.e., the nearest neighbor particles. Further, although a weak gravitational confinement was introduced to maintain large surface-particle density in the central region of the sample, the central region is large and flat. Therefore, we neglect gravity and the curved interface near the well edge in our analysis; had the curvature of LC surface within the field-of-view been significant, then the interparticle separations would have varied smoothly within the field-of-view.¹⁶ By sampling over the full field-of-view and checking the pair correlation functions, we confirmed that no systematic tendency exists for variation of interparticle separation, r. Currently, we have no evidence to indicate that other interparticle attractions exist in our system, e.g., other interactions that have been discussed and debated in previous work.13,14,17,18,67

Combining data from different temperatures, we plot the effective spring constant *versus* interparticle distance (Fig. 5). Note, we plot $\kappa_{\text{eff}} T/K$ *versus* r; the temperature T and the elastic coefficient K are included to normalize temperature effects that arise between data from different measurements



Fig. 5 The effective spring constant $\kappa_{\rm eff}$ (together with corresponding normalization factors *T* and *K*) between adjacent particles for the lowest five temperatures in Fig. 3(d) is plotted as a function of interparticle separation *r*. The orange crosses exhibit raw data, and the black error bars represent the average $\kappa_{\rm eff} T/K$ values, standard deviations (thin lines), and standard errors (thick lines) within each 0.1 pixel bin with a filtering condition that insures only bins with more than 400 data points are recorded. Inset: The binned data is re-plotted with both axes logarithmically scaled. Grey shadow region shows the best linear fit, a power law of -3.43 2.41. The quadrupole only (-7, blue dashed line) and dipole only (-5, red solid line) power laws are also presented.

(see Section 3.4 for *K* values used). Also, since we observed deviations from linear correlation between \mathfrak{D} and T/η_1 when the temperature approached the nematic–isotropic transition, we only include data for the lowest five temperatures in Fig. 3(d).

Previous experiments on this system class measured the interaction between two isolated particles with optical tweezers.¹⁶ Here we aim to use displacement correlations to quantitatively demonstrate the dominant form of interaction between colloidal particles in the dense packings at the air-NLC interface. Unfortunately, as shown in Fig. 5, the dynamic range of particle separation, r, is quite small. Thus, differentiation between various interaction models (power laws, see Fig. S3 in ESI† for detail) using these data is very difficult. In the plot we show the best fitting which gives a power law with exponent of -3.432.41. Power laws of -5 and -7 arising, respectively, from dipole-only and quadrupole-only interactions lie within the error bars of our data. Therefore, the data is not of sufficient quality to make claims about the form of the interaction between particles; neither the simple dipole form, nor the simple quadrupole form, nor other complex forms convincingly describe the data. We must leave such determinations to future work which can acquire data offering a much larger dynamic range of r.

3.4 Spring constant as a function of temperature

Though we were unable to determine the exact form of the interparticle potential, our experimental measurement still enables investigation of the temperature dependence of κ_{eff} and σ_t/r . We explored these variations with temperature. The average value of the spring constant, κ_{eff} , was obtained from data at each temperature as the system evolved towards the nematic–isotropic transition. The blue squares in Fig. 6(a) show

that the stiffness of effective springs decreases with increasing temperature in this range. Note, the vertical "error bars" do not represent measurement errors; rather, they are the standard deviation of $\kappa_{\text{eff}(j)}(T)$ when fitted to a Gaussian distribution. σ_t/r is also expressed as a function of T (green circles) and is shown to decrease in magnitude as temperature increases.

Quantitatively, κ_{eff} is the second derivative of the potential energy of the spring on bond *b* while σ_t/r is the derivative of potential divided by interparticle separation.⁴⁰ Since the potential is proportional to the temperature-dependent elastic coefficient *K*,^{63,68} the spring constant κ_{eff} (as well as the stress term σ_t/r) is expected to be temperature-dependent.

The LC's effective spring constant is proportional to *K*. Previous work provides experimental data which exhibits an approximate relation between elastic coefficients and temperature. The primary results are expressed through the dependence of the splay (K_{11}), twist (K_{22}), and bend (K_{33}) elastic coefficients of 5CB as a function of the order parameter *S*,²⁰ which in turn depends on temperature:²⁴

$$K_{11} = 5.98 \qquad S^{2.15} \tag{7}$$

$$K_{22} = 2.70 \qquad S^{1.96} \tag{8}$$



Fig. 6 (a) Our measurement of the average stiffness of the effective spring, κ_{eff} , is shown with the blue squares as a function of temperature. The green circles show the stress term, σ_t/r , as a function of *T*. (b) κ_{eff} data is re-plotted; the dark-red dashed curve gives the one-constant approximated elastic coefficient, *K*, *versus* temperature following eqn (7)–(10). Experimental measurements of *K* from previous work are also reproduced on the plot as black dotted curves.^{20–24}

$$S = \leftarrow 1 - \frac{T}{T_{\rm NI} + 0.25} \quad (10)$$

We employ the one-constant limit of the Frank free energy to keep the calculation simple.⁶³ A single elastic coefficient of 5CB, K, may be used in the theory; in practice, we use the arithmetic mean of 5CB splay, twist, and bend elastic coefficients for K. Note, in our system, the LC twist likely has only a minor effect. Thus, another possible way to do these calculations is to neglect K_{22} and take the arithmetic mean of K_{11} and K_{33} to derive K(T). This latter approach causes K to increase by a factor of ≈ 1.3 . It does not alter the main observed trends, but it will change the fitted coefficients for the potential.

Following eqn (7)–(10), we plot the one-constant approximated elastic coefficient *versus* temperature as the dark-red dashed curve in Fig. 6(b). The figure again shows our experimental spring constant data (κ_{eff}) *versus* temperature for reference. Since measurements of the elastic coefficients of 5CB vary somewhat for those reported in previous publications, we also reproduce the experimental measurements from different work^{20–24} as black dotted curves in the plot. Comparing the general tendencies of these curves, the positive correlation between κ_{eff} and *K* is apparent.

This result can be understood qualitatively when one considers the effect temperature has on the nematic order and elastic energy of the LC. As the temperature increases, the nematic order and elastic energy of the LC decrease. As the nematic order and elastic energy decrease, the interaction between particles mediated by the LC medium weakens, *i.e.*, the effective spring constant between particles decreases.

Here we use the temperature dependence of elastic coefficients to explain our observations about the behavior of the temperaturedependent effective spring constant. Alternatively, this general formalism provides an approach to assess the value of *K*. For example, when the exact potential form (*i.e.*, the relation between κ_{eff} and *K*) are resolved *via* the method described in Section 3.3, then a simple computation *via* the covariance procedure can lead to measurement of LC elastic coefficient. Notice, however, almost all current theories employ the one-constant limit of the Frank free energy; thus this method provides average *K* instead of individual K_{11} , K_{22} , and K_{33} .

4 Conclusions

We have created self-assembled monolayers of particles at the air–NLC interface and have analyzed the diffusion and vibrational phonon modes of crystalline packings of colloidal particles. These measurements provide quantitative insight about the LC-defect-mediated interparticle interaction effects. On short timescales, the particles exhibited diffusive motion with diffusion coefficients consistent with a Stokes–Einstein model wherein the effective viscosity is predominantly that of 5CB. The phonon density of states (DOS) exhibited Debye scaling at low frequencies and van Hove-like singularities at higher frequencies. The dispersion relations for transverse and longitudinal vibrational modes, and their corresponding sound velocities, were also calculated. Moreover, the dependence of these interactions on particle separation was quantitatively analyzed, but the data did not permit accurate determination of potentials. Finally, the temperature dependence of these interparticle forces was consistent with expectations based on previous (temperaturedependent) measurements of the splay, twist, and bend elastic moduli.

Looking to the future, the 2D system we have created and studied offers new ways to explore interesting questions. For example, with improvements and larger system size, it should be possible to investigate phase transitions and possible hexatic states in a new class of 2D crystal mediated by elastic defects that penetrate asymmetrically into the surrounding media. In a different vein, using other types of LCs or particles, it should be possible to create situations wherein the particles submerge less into the LC; in this case, variation in particle diffusion will be interesting to study. More work is needed to understand the phonon DOS variation with temperature, which at least partially reflects quenched disorder (albeit while maintaining the hexagonal lattice); this scenario potentially offers an experimental technique for study of connections between phonon spectra and disorder. Finally, experiments with better signal-to-noise, for example due to larger dynamic range of particle separations, are needed for precise determination of interparticle potentials. Setups such as a wedge-shaped well could be employed for this purpose. The ability to vary lattice spacing provides us with the possibility to check for attractive interactions and to investigate how crystal vibrational behavior is altered by different interparticle separations.

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Paper

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