Liquid-crystal mediated nanoparticle interactions and gel formation

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Colloidal particles embedded within nematic liquid crystals exhibit strong anisotropic interactions arising from preferential orientation of nematogens near the particle surface. Such interactions are conducive to forming branched, gel-like aggregates. Anchoring effects also induce interactions between colloids dispersed in the isotropic liquid phase, through the interactions of the pre-nematic wetting layers. Here we utilize computer simulation using coarse-grained mesogens to perform a molecular-level calculation of the potential of mean force between two embedded nanoparticles as a function of anchoring for a set of solvent conditions straddling the isotropic–nematic transition. We observe that strong, nontrivial interactions can be induced between particles dispersed in mesogenic solvent, and explore how such interactions might be utilized to induce a gel state in the isotropic and nematic phases. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4802774>]

I. INTRODUCTION

Colloidal particles dispersed into a nematic liquid crystal phase impose defects on the nematic through local ordering interactions with the colloidal surface. As these depend on the nematic director as well as the local surface topography, such interactions are anisotropic. When strong, such interactions may result in colloidal gelation, a phenomenon by which macromolecular objects assemble into large space-spanning aggregates through non-covalent bonding. These physical gels, materials distinct from covalently bonded chemical gels, can be assembled through a large palette of forces, including van der Waals, electrostatic, and depletion interactions. The strength of the interactions and the effects of gravitational compaction determine the density and mechanical properties of the resulting colloidal gel.^{1–6} These gels form when particles become arrested on their way to an equilibrium conformation, which is often the desired state (e.g.) when assembling a colloidal crystal. Gelation can be a desirable phenomenon, used to control the response of a colloidal suspension, to improve shelf-life and texture of foods or other materials. In the case of colloid–liquid crystal (LC) mixtures, gelation is a method by which the mechanical response of the soft colloidal network can be merged with the optical response of a liquid crystalline material. The resulting materials have a wide variety of possible applications from displays to liquid-crystalline semiconductors⁷ to sensors. Systems coupling physical gels with liquid crystalline systems have been prepared using physical and chemical gelators^{7,8} at the molecular level, with a gel structure determined by the relative temperatures of gelation, T_{gel} and the isotropic–nematic (IN) phase transition T_{IN} . Systems which gel above the IN transition exhibit a random network structure, while systems gelling below this transition experience

phase separation into filaments aligned with the nematic director.⁷

For sterically stabilized colloids or nanoparticles, aggregation arises through interaction of particles with the mesogenic solvent.⁹ Previous experimental investigations of colloid–LC mixtures^{9–17} posit different mechanisms and structures for gelation, depending on the nature of dispersion. When colloids are dispersed in an isotropic LC phase, cooling of the liquid below the IN transition temperature favors the nucleation of nematic droplets within the mixed phase. As the presence of colloids within this phase creates defects,¹⁸ free energy is minimized by expelling colloids from the growing nematic droplets. This results in a system whose shear modulus increases dramatically at the IN transition temperature, as a foam-like cellular structure emerges due to demixing.^{10,11} By contrast, a gel may also be formed by colloids dispersed into a nematic liquid, though the structure in this case is more fractal in nature.¹³ The mechanism for formation of such a gel is also dramatically different. Anchoring at the colloidal surface creates defects (such as dipolar hedgehog, or quadrupolar boojums and Saturn rings^{18,19}). Rather than expelling the colloidal particles from the nematic completely, the system minimized free energy by driving colloids toward each other.^{20–32} For degenerate planar anchoring, this results chaining of particles at 30° to the nematic director, as the overlapping defect regions minimize the global free energy.^{23,24} For nondegenerate planar or homeotropic anchoring, pairs of particles will tend to also assemble linearly, with a minimum in free energy at a pair orientation parallel to the nematic director.²² For the case of Saturn-ring defects, higher order coordinations can occur,^{21,29,33} and the combined overlap of these leads to kinetic arrest.¹³

In each of these cases, the formation of a colloidal network is inherently coupled to the isotropic–nematic transition. It is desirable to decouple these phenomena in order to create tunably rigid, optically responsive materials.

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Anchoring within the isotropic phase is known to create nematic wetting layers or coronas, whose interactions have attractive and repulsive characters.^{18,34–43} The range of this interaction can be characterized by the thickness ξ_w of the nematic wetting layer, which diverges as coexistence is approached.³⁶ The prevalence of wetting is strongly dependent on the curvature of the wet surface—prewetting behavior is expected to disappear entirely for particles with radii less than 100 nm.³⁶ The overlap of nematic coronas is predicted to result in a strong attraction having a Yukawa-like dependence for $a \gg \xi_w$.³⁵ The range and strength of the interaction are easily tunable by changes in temperature around the IN transition,^{35,41} and can induce flocculation^{40,42,43} (and potentially physical gelation) of these particles. Though these models offer predictions for the attraction strength in the limit of small particles, this limit is largely unstudied in the literature. Previous investigations^{21,27,44,45} of nanoparticle interactions have focused primarily on the strong anchoring limit, valid for micron-sized particles, but inappropriate for simulations of nanoparticles, where binding of mesogens is expected to be much weaker due to curvature considerations.^{22,46} To this end, we investigate how one might utilize various surface anchorings, and the pre-nematic wetting layers they induce, in order to assemble nanoparticles within the isotropic phase, using coarse-grained molecular simulations. Studies which have accounted for variable anchorings^{22,47} used continuum models, unable to resolve any molecular details which may be of importance in nanoparticle interactions. A previous investigation including such molecular detail²⁰ focused on homeotropic interactions in the strong coupling limit, finding a weak attraction ($\approx k_B T$) between two nanoparticles in the isotropic phase, with a deep minimum ($\approx 10 k_B T$) within the nematic phase. Few other molecular simulations exist, though a notable set of investigations involving soft spherocylinders under conditions of weak homeotropic and planar anchorings, primarily focused on interactions within the nematic phase.⁴⁸ These latter simulations observed

interactions within the isotropic phase to be repulsive, except for depletion interactions at close separations; interactions within the nematic phase were found to have an attractive interaction whose strength was dependent on the nematicity of the solvent.⁴⁸ Here, we explicitly investigate a range of anchorings from strongly planar to strongly homeotropic and examine how these interactions change upon transition between isotropic and nematic phases. Through examination of a variety of anchoring conditions, we develop a coherent picture of how liquid-crystal mediated assembly of nanocolloids may proceed within the isotropic phase.

II. METHOD

We perform molecular dynamics simulations of coarse-grained mesogens in the NVT ensemble^{49,50} using a modified version of the LAMMPS simulation package.^{51,52} Our primary interest in these simulations is elucidating the effect of mesogen anchoring on the pair interaction of two suspended nanoparticles. These simulations are performed on a molecular scale, with our exploration of phase space facilitated through the use of coarse-grained potentials, such as the Gay-Berne (GB) potential,^{53,54} coupled with metadynamics^{55,56} performed on variables of interest.

A. Gay-Berne potential

The Gay-Berne potential^{53,54,57,58} is a modification of the standard 12-6 Lennard-Jones potential to prolate and oblate ellipsoidal particles. This is effective for modeling mesogenic systems, as it encompasses asymmetries in shape and orientational affinity that arise between liquid crystal molecules. The shape-dependent piece of the GB interaction is derived by considering the overlap of multidimensional Gaussians with the same symmetries as the mesogens.^{53,57} To facilitate the discussion below, we will define the function

$$\Gamma(\omega, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = 1 - \omega \left[\frac{(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}}_{ij})^2 + (\hat{\mathbf{u}}_j \cdot \hat{\mathbf{r}}_{ij})^2 - 2\omega(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{u}}_j \cdot \hat{\mathbf{r}}_{ij})(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)}{1 - \omega^2(\hat{\mathbf{u}}_i \cdot \hat{\mathbf{u}}_j)^2} \right], \quad (1)$$

which appears in both the distance and energy formulas. In this expression ω is a dummy variable which acts as a placeholder for physical ratios separately defined for each function. Compactly, we may write the potential as

$$U_{GB}(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = 4\epsilon_0 \epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) [\Xi^{-12} - \Xi^{-6}], \quad (2)$$

where the surface-surface distance between the particles is approximated by the function

$$\Xi = \frac{r_{ij} - \sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) + \sigma_0}{\sigma_0}. \quad (3)$$

Here σ_0 is the diameter of the particles in the cross section normal to their axis of orientation, and the parameter ϵ_0 sets the energy scale of the potential. Molecular anisotropy is included in the potential through the energy modulation function

$$\epsilon(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = [1 - \chi^2(\hat{\mathbf{u}}_j \cdot \hat{\mathbf{u}}_i)]^{-\frac{\nu}{2}} [\Gamma(\chi', \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij})]^\mu, \quad (4)$$

and the molecular shape function

$$\sigma(\hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = \sigma_0 \Gamma(\chi, \hat{\mathbf{u}}_i, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}). \quad (5)$$

FIG. 1. Interaction potential for Gay-Berne mesogens using the parameters $(\kappa, \kappa', \mu, \nu) = (3, 5, 2, 1)$ in the notation of Ref. 59. The configurations correspond to end-to-end (—), end to side (---), crossed ($\times$), and side-to-side (||) arrangements. Crossed mesogens have an interaction equivalent to Lennard-Jones spheres with $\epsilon = 1$ and $\sigma = 1$.

The parameters χ and χ' depend on the aspect ratio $\kappa = \sigma_e/\sigma_s$ and energy ratio $\kappa' = \epsilon_e/\epsilon_s$ for end-to-end (e) and side-to-side (s) conformations as

$$\chi = \frac{\kappa^2 - 1}{\kappa^2 + 1} \quad (6)$$

and

$$\chi' = \frac{\kappa'^{1/\mu} - 1}{\kappa'^{1/\mu} + 1}, \quad (7)$$

respectively.

The description of this system is facilitated greatly through the identification of useful dimensionless units and simple parameterizations.^{49,50} The most natural unit length in this system is the minor diameter σ_s , which we identify henceforth with σ_0 . Energy, similarly, is identified with the parameter ϵ_0 . Together, these define the reduced temperature $T^* = k_B T/\epsilon_0$, velocity $v^* = v/\sqrt{\epsilon_0/m}$, and time $t^* = \sqrt{\epsilon_0/m\sigma_0^2}$. Henceforth we will use these and further naturally derived reduced units tacitly. Importantly, because of these unit quantities, only four parameters are necessary to specify the GB model at fixed NVT . In the compact notation of Ref. 59 these are $(\kappa, \kappa', \mu, \nu)$, which are set to the well-studied set $(3, 5, 2, 1)$ ^{60,61} in our simulations. A plot of the mesogen-mesogen interactions at four characteristic arrangements is given in Fig. 1.

The Gay-Berne interaction as stated here is valid only for a one-component system comprised of uniaxial particles. Extensions of the overall potential to biaxial mesogens also exist, allowing for the specification of ellipsoidal particles of completely arbitrary shape,⁵⁷ though we do not consider these here. A further extension to mesogens of different size and attraction characteristics was introduced by Cleaver and co-workers in Ref. 58. This allows one to adapt the simple GB model to mixtures of more than one type of mesogen, or of mesogens and spherical particles, which we will discuss in Sec. II B.

B. Anchoring conditions

Anchoring in colloid-mesogen mixtures can be achieved in two ways. One follows the prescription of Ref. 58, taking the limit of the mixed mesogen-mesogen interaction as the anisotropy coefficient κ of the second species goes to one. A problem with this prescription is that the decay of the potential is given by the effective colloid-mesogen diameter, which is on average $R + \kappa\sigma/2$, where R is the nanoparticle radius. For strong anchoring conditions, very long ranged orientational interactions result that create wetting layers that may be several major diameters thick. We find this to be unrealistic, and instead opt for the method of Ref. 62, which integrates the orientation-based interaction of a single mesogen and a plane of Lennard-Jones spheres with diameter σ_0 . This results in a much narrower minimum (cf. Fig. 2) more appropriate to the limits of larger nanoparticles. Though for the spheres embedded in our LC, R is only $2\sigma_0$, we expect that the short-ranged anchoring potential will allow qualitative conclusions about how LC anchoring influences pair interactions phenomena in systems of larger particles.

For clarity in the discussion below, we regard the mesogen as particle j and the colloid as particle i . Further, we make use of the dimensionless forms outlined in Sec. II A. Similar to the case for mesogen-mesogen interactions, anisotropy in colloid-mesogen interactions is captured through a function,

$$\tilde{\Gamma}(\omega, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = \frac{1 - \omega}{1 - \omega[1 - (\hat{\mathbf{r}}_{ij} \cdot \hat{\mathbf{u}}_j)^2]}, \quad (8)$$

which appears in the excluded volume and energy modulation terms. Noting the surface-to-surface distance,

$$\xi_{ij} = r_{ij} - R - \tilde{\Gamma}(\chi, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}), \quad (9)$$

we may write the full potential as

$$U_{CM}(\hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) = \epsilon_{CM} \tilde{\Gamma}(\chi'_{CM}, \hat{\mathbf{u}}_j, \hat{\mathbf{r}}_{ij}) \left[\frac{1}{45} \left(\frac{1}{\xi_{ij}} \right)^9 - \frac{1}{6} \left(\frac{1}{\xi_{ij}} \right)^3 - \frac{1}{40} \left(\frac{1}{r_{ij}} \right) \left(\frac{1}{\xi_{ij}} \right)^8 + \frac{1}{4} \left(\frac{1}{r_{ij}} \right) \left(\frac{1}{\xi_{ij}} \right)^2 \right]. \quad (10)$$

The remaining unspecified parameter, χ'_{CM} depends on the ratio of side-on (s) to end-on (e) mesogen colloid interactions,

$$\chi'_{CM} = 1 - \left(\frac{\epsilon_s}{\epsilon_e} \right)^{-1/\mu}. \quad (11)$$

In the unitless description above, we may specify a scalable class of models for the anchoring interactions exactly through three parameters—the colloid radius R , the strength ratio ϵ_s/ϵ_e , and the overall strength ϵ_{CM} . Table II gives

FIG. 2. Surface anchoring potential of Gay-Berne mesogens to nanoparticle surfaces for the parameter sets listed in Table II. The planar anchoring potential is plotted with lines, while symbols of the same color are used for homeotropic anchoring. For clarity, each sequential parameter set is offset from the previous by $k_B T$. Dashed zero-potential lines are included to guide the eye.

parameters for the anchoring conditions used in our simulations to induce strong planar, planar, equivalent, homeotropic, and strong homeotropic anchorings. We fix the radius for these investigations at $R = 2$. Due to the nature of the potential, the planar anchoring condition is degenerate, and will follow the direction of the local nematic director (if present). Due to the choice of potential in our systems, anchoring is a consequence of two inseparable effects. The first is an adsorption affinity for mesogens to the colloid surface characterized by the potential strength parameter ϵ . Increasing the value of ϵ , without considering other effects, will enhance the probability of finding mesogens at the surface of the colloidal particle. The second piece is the relative orientational affinity, controlled by χ'_{CM} . This determines the relative ratio of planar to homeotropically oriented mesogens at the colloid's surface. Note that setting $\epsilon_e = \epsilon_s$, which we will refer to as *equal anchoring*, gives rise to a slight mismatch in well depths, though for the parameters we choose each is weak ($< k_B T$) and should not engender significant anchoring preference. Since the potential is short-ranged, any enhanced adsorption caused by the choice of large ϵ only serves to enhance the anchoring conditions on the colloidal surface, and thus there should be no ambiguity about the consequences of our potential choice.

With the mesogen and anchoring potentials given, the only unspecified piece is the colloid–colloid interaction. Here we use a Lennard-Jones potential with strength ϵ_0 and diameter $2R$ that has been shifted and truncated so that it becomes purely repulsive. In this way, we may be certain that any attractive features of the measured interactions are solely due to liquid-crystal structure around the colloidal surfaces.

C. Metadynamics

Diffusion of spheres in a dense solvent of mesogens is computationally slow, involving the resolution of many timescales. Since our chief interest is in equilibrium behavior, rather than instantaneous dynamics, we may take advantage of methods with unphysical dynamics in order to obtain equilibrated states and thermodynamic averages. One

such method is metadynamics,⁵⁵ a molecular-dynamics implementation of a more general class of flat-histogram methods (for reviews, see Refs. 63 and 64), which can be used to obtain the free energy of a system as a function of one or more order parameters or reaction coordinates. Previous investigations in this group have utilized the conceptually similar expanded-ensemble density of states method (EXEDOS) to obtain colloid–colloid²⁰ and colloid–wall^{65,66} potentials of mean force from Monte Carlo simulations. Both EXEDOS and metadynamics proceed through the deposition of a history-dependent bias, steering a system away from free energetic basins, accelerating the sampling of the equilibrium density of states.

We utilize metadynamics for two purposes—equilibration of mesogenic order, and determination of the colloidal potentials of mean force (PMFs). Initially, we apply metadynamics to the nematic order parameter,

$$S = \left\langle \frac{3}{2} P_2(\hat{\mathbf{n}} \cdot \hat{\mathbf{u}}_j) - \frac{1}{2} \right\rangle, \quad (12)$$

where $\hat{\mathbf{n}}$ is the nematic director, and $\hat{\mathbf{u}}_j$ is the orientation of particle j , which is averaged over in the ensemble. This allows the efficient generation of randomized initial conditions for each density of interest. A system at the equilibrium order parameter $S(\rho^*, T^*)$ for a particular temperature–density state point may be obtained efficiently by perturbation of any accessible system configuration. The accumulation of Gaussian biases in the metadynamics method drives a system toward its global free-energetic minimum more efficiently than standard molecular dynamics.

For these simulations (in the NVT ensemble, utilizing a Langevin thermostat), particles are initialized on a lattice, melted at a temperature $T^* = 10.0$, and subsequently quenched to a temperature $T^* = 1.0$. The order parameter entering a metadynamics simulation is thus isotropic. The number of particles N is varied in order to achieve densities ρ in the range $[0.264, 0.356]$. Metadynamics parameters for these simulations are given in Table I, and the resulting free energies are plotted in Fig. 3. Our results clearly identify an isotropic–nematic transition occurring within this range, commensurate with the results in Ref. 60.

We identify from these simulations a set of density conditions spanning the isotropic–nematic transition, $\rho^* = \{0.264, 0.279, 0.294, 0.321\}$, by locating systems whose free-energetic minima lie around the threshold value $S = 0.3$ (cf. Fig. 3). This point determines the approximate equilibrium order parameter $S_{eq}(\rho^*, T^*)$. Systems with $S_{eq} < 0.3$ are considered isotropic, while simulations with a larger S_{eq} are considered nematic. While a detailed study of the

TABLE I. Metadynamics parameters for nematic order parameter and potential of mean force simulations. The pseudotemperature ΔT is an additional parameter used in well-tempered metadynamics (cf. Ref. 56), such as the simulations performed here. For further details, see the text.

Order parameter	Gaussian height (ϵ)	Gaussian width	ΔT (ϵ)
S	10.0	0.02	10.0
PMF(r)	10.0	0.10	10.0

FIG. 3. Free energy as a function of order parameter for various densities obtained through metadynamics. Pictured are densities ρ^* from 0.264 to 0.356, with the six values $\rho^* = \{0.264$ (open squares), 0.279 (solid squares), 0.294 (open triangles), 0.321 (closed triangles), 0.338 (open diamonds), and 0.356 (solid diamonds)) emphasized using points for clarity. A total of 30 independent runs, including three duplicates for each density, are shown. The first four highlighted densities are utilized to obtain potentials of mean force in later simulation.

Gay-Berne phase behavior is beyond the scope of our paper, we note that one may also obtain the IN transition temperature in our simulations as giving a free energy curve with equal depths at values of S above and below our designation. None of the densities studied exhibits such obvious bimodality, though the densities $\rho^* = \{0.294, 0.321\}$ each has a secondary minimum corresponding to the more or less ordered state, respectively.

Following determination of the equilibrium ordering, representative configurations are sampled for each LC density. These simulations proceed by removing all mesogens which overlap with placed nanoparticles, and simulating for a few thousand timesteps in order to equilibrate velocities and allow particles near the colloidal surface to anchor. Metadynamics is then performed on the separation of the two colloidal particles to obtain the potential of mean force between them. Parameters for these metadynamics runs in terms of Gaussian heights, widths, and pseudotemperatures are given in Table I. The PMF systems are performed with a wall on the order parameter that prevents sampling of separations beyond 15σ .

III. RESULTS

PMF simulations are obtained via metadynamics runs on the nanoparticle center-to-center separation in the NVT ensemble. All simulations take place at temperature $T^* = 1.0$ in a cubic box with volume $(30\sigma)^3$. Periodic boundaries are utilized to mimic bulk conditions, with the minimum image convention to calculate neighbor interactions. Following equilibration of the nematic, we add a pair of colloids into each simulation box. For each of the four densities, we study three independent realizations of five different sets of anchoring parameters corresponding to strong planar anchoring, planar anchoring, equal anchoring, homeotropic anchoring, and strong homeotropic anchoring. Anchoring

conditions lead to local preferences for the orientation of mesogens. In the isotropic phase, this creates a pre-nematic wetting layer with strong radial or planar orientational ordering near the particles' surface. Radial orderings will be defect free, while planar orderings must have two surface defects, a consequence of the Poincaré–Hopf theorem. In the nematic phase, homeotropic anchoring results in dipolar or “Saturn-Ring” quadrupolar defects,¹⁸ while degenerate planar anchoring results in quadrupolar Boojum defects on the polar axes of the particle.

Interactions within the nematic phase are complex, but have minima near contact, where the defect structures overlap and join to minimize global free energy. It is unclear what interactions take place inside the isotropic phase, though a weak attraction has previously been predicted for the case of strong homeotropic anchoring²⁰ when the ordered mesogen layer on each surface is shared. Ostensibly one would expect attractive interactions between nanoparticles whose surface ordering structures overlap. In the case of shared surface layers, these interactions are potentially very strong. In Secs. III A–III C, we examine the five sets of anchoring conditions listed in Table II in detail.

A. Equal anchoring

We begin with a system exhibiting equal energies for homeotropic and planar anchoring, labeled as System I in Table II. Each orientation has a weak affinity for the nanoparticle's surface, which will result in slight adsorption of particles to the surface, though no preferred structure is expected at the surface of the molecule. Examining the PMF (Fig. 4), we find that it is featureless at large separations, as is expected for interactions within an isotropic fluid. Any defects present at the surface of these particles should be transient and extremely short-ranged. As the particles are moved closer together, structure in the fluid becomes apparent. Particles experience a weak repulsion, commensurate with a loss of configurational entropy, as they are brought closer together. This behavior is echoed within the nematic phase, though interactions are less repulsive at small separations.

As their separation decreases to 7σ ($=2R + \kappa\sigma$), nanoparticles in both isotropic and nematic fluids experience a significant ($\approx 2k_B T$) repulsion as the last layer of solvent is squeezed out from between the two spheres. This repulsive barrier occurs at around 5σ , which is a large enough separation that the sphere–sphere repulsion is very weak, suggesting its origin lies in solvent structure at the particle surfaces. After this peak, each system gives way to a strong attractive

TABLE II. Anchoring parameters for PMF simulations.

Label	ϵ	ϵ_e	ϵ_s	$\beta U_{\min}^{\text{side}}$	$\beta U_{\min}^{\text{end}}$
I	4.0	1.0	1.0	−0.4544	−0.3501
II	100.0	1.0	20.0	−8.6749	−0.5677
III	22.0	1.0	5.0	−1.9095	−0.4993
IV	4.0	1.0	0.2	−0.3471	−2.2713
V	4.0	1.0	0.05	−0.3486	−9.0841

FIG. 4. Potential of mean force as a function of center-to-center separation for equivalent planar and homeotropic anchoring depths at the surface of the nanoparticle (cf. System I in Table II). Densities $\rho^* = 0.264, 0.279, 0.294$ lie in the isotropic regime, while $\rho^* = 0.321$ is nematic (cf. Fig. 3).

minimum which occurs inside the overlap region of the two soft spheres. Since both solvent and solute have excluded volume interactions, this minimum is due primarily to depletion-like interactions,⁶⁷ a conclusion supported by the strong density dependence observed in the depth of these minima.

Interestingly, these results suggest that even neutrally anchored particles within a LC solvent can experience significant forces due to solvent structure. This interaction is repulsive down to $\approx 5\sigma$ separation in the isotropic phase, with weaker repulsions occurring within the nematic phase. In an experimental system, one can expect the primary minimum seen in these systems to be strongly mitigated by steric hindrance, along with the presence of a kinetic barrier due to liquid structure, making the formation of gels in the isotropic phase unlikely. This suggests that neutrally anchoring particles will tend to remain dispersed in a LC phase, rather than separating into a particle rich liquid or solid phase.

B. Planar anchoring

If anchoring is modified, so as to induce weak planar anchoring at the nanoparticle surface, new features appear in the PMF. We begin by examining the case of weak planar anchoring plotted in Fig. 5 (cf. System II in Table II). Just as in the equal anchoring case, the free energies are essentially flat at the maximum distances considered, though here, the presence of a slight slope belies an apparent weak, long-ranged repulsion in the isotropic fluid phase. Such repulsion is reminiscent of that seen in systems of planar anchoring nanoparticle-spherocylinder mixtures.⁴⁸ For these isotropic fluids, again a repulsive barrier appears as particles are brought closer together. This barrier is enhanced relative to the equal anchoring case due to the increased ordering within the liquid crystal near each particle's surface. Again, a weak dependence on density is observed, suggesting that this barrier corresponds to the free energy required to squeeze fluid layers out from between the nanoparticles. This is supported by the positions of a weak repulsive peak at a center-to-center distance of $2(R + \sigma)$, corresponding to independently adsorbed surface layers

FIG. 5. Potential of mean force for weak planar anchoring at the surface of a nanoparticle (cf. System II in Table II).

on each particle, and a stronger ($\approx 5k_B T$) peak at $2R + \sigma$, corresponding to squeezing out the last layer. Beyond this point, a primary depletion minimum is also seen.

For the nematic phase, both the primary minimum and the two barriers are present, but these are accompanied by a slight attractive preference for these particles on either side of the two layering maxima. We anticipate that these correspond to independently adsorbed layers that are favorably interacting due to the nematic field at $R = 6.5\sigma$, and a similar effect for shared layers at $R = 5.5\sigma$. This conclusion is supported by the observance of similar features in isotropic solvent. The attraction strength at each minimum is a few $k_B T$. Another potential explanation for the attractive well is the overlap of Boojum defects for the degenerate colloidal particles. As our method is unable to obtain the orientation of surface defects relative to the nematic director, it is unclear to what extent this contributes. An attractive minimum for these particles is expected, on the basis of continuum theory, to occur at contact.^{22,24}

As noted, the positions of these attractive regions line up with similar features for isotropic LC phases, albeit ones which define states metastable relative to the bulk. For high enough concentrations of nanoparticles, reduced entropy at large separations may be enough to drive particles into these weak secondary minima, meaning the planar pre-nematic layer can potentially induce gelation at high enough particle concentrations. Such a system was studied previously via simulations in the nematic state,¹³ though it was concluded that planar anchoring was insufficient for the formation of a particle gel.

Examining the strong planar anchoring conditions (cf. System III in Table II), we obtain markedly different PMFs, plotted in Fig. 6. Here, the strongly oriented, adsorbed layers prevent overlap, and thus the appearance of a primary minimum. Near contact, the features mimic those in the weak anchoring case, with a sequence of undulations corresponding to fluid layers being expelled from between the nanoparticles. Though the overall structure of the PMF is similar, the behavior is strongly nonmonotonic. A flat profile in the isotropic phase at first rises with density from $\rho^* = 0.264$ to $\rho^* = 0.279$, signifying growing repulsion between particles.

FIG. 6. Potential of mean force for strong planar anchoring at the surface of a nanoparticle (cf. System III in Table II).

Further increase of the density results in the appearance of a long-ranged weak attraction with minimum around $r = 8\sigma$. Note that at this separation, it is likely that pre-nematic wetting layers are overlapping, rendering increased stability to these conformations. As boojums are free to rotate around particles in the nematic phase, such attractions can support many particle contacts. As the depth of the attraction is $\approx 2k_B T$, such interactions may facilitate formation of long-lived colloidal gels. Increasing the density further to favor a global nematic phase at $\rho^* = 0.321$ renders the interaction again globally repulsive. This suggests that though strong planar anchoring may create a gel in the isotropic phase near the isotropic–nematic transition, strong planar anchorings are unable to create structure in the nematic phase, in agreement with the results of Ref. 13.

C. Homeotropic anchoring

Finally, we examine the case of homeotropic anchoring. In the weaker homeotropic case studied (cf. System IV in Table II), plotted in Fig. 7, we see several features begin to appear in addition to the equal-anchoring PMF (Fig. 4). A flat profile at large separations shows a dip at $\approx 8\sigma$ for all densities studied, indicative of an interaction of the defect re-

FIG. 7. Potential of mean force for weak homeotropic anchoring at the surface of a nanoparticle (cf. System IV in Table II).

gions. This distance is $\approx 2(R + \kappa\sigma)$, and likely corresponds to a weak sharing of the homeotropic anchoring at the surface of the nanoparticle. Outside this distance, the PMF is featureless for $\rho^* = 0.264$ and $\rho^* = 0.279$, though a weak repulsive barrier for $\rho^* = 0.294$ signals the transition from two independently adsorbed layers to a single layer. Inside, a strong barrier to aggregation is present, mimicking results for weak planar anchoring.

Within the nematic phase at $\rho^* = 0.321$, interactions are initially repulsive when spheres approach, with undulations that recall previous work on homeotropically anchoring nanoparticles.²⁰ Attractions that are observed as minima in the PMF are, however, apparently metastable for these anchoring conditions, with the entropically favorable large separations yielding similar free energy. All attractive regions excluding the primary minimum have depth $\lesssim k_B T$.

Finally, we examine the case of strong anchoring (cf. System V in Table II), plotted in Fig. 8. This is the system most commensurate with recent continuum nanoparticle studies. At this strength each nanoparticle has a halo of mesogens tightly bound around its surface. Repulsive and attractive features in these plots correspond primarily to the interactions of these bound layers with interstitial fluid. Within the isotropic phase, we find three regions with essentially non-monotonic behavior. At the lowest density, the PMF experiences a repulsive barrier at 14σ and another at 11.5σ , corresponding to $2R + 3.5\kappa\sigma$ and $2R + 2.5\kappa\sigma$, respectively. This is followed by a strong minimum ($\approx 5k_B T$ relative to the height of the previous barrier) as the halos approach, near $r = 2(R + \kappa\sigma)$. Beyond this, particle halos must be disrupted for the nanoparticles to move closer together, a fact which is reflected in the large free energy barrier to closer approaches.

At density $\rho^* = 0.279$, similar features are observed in the fluid phase. A second, weakly attractive oscillation occurs in the PMF at $r = 13.5\sigma$. The attractive minimum occurring at $r = 2(R + \sigma\kappa)$ has subsequently deepened by an amount $\approx k_B T$, with the repulsive barrier remaining at the same height. The higher density appears to force tighter binding of mesogens to the nanoparticles, resulting in this shift. Beyond $r = 2(R + \kappa\sigma)$ a steep potential increase is again met, though there is an indication of a metastable state at this density

FIG. 8. Potential of mean force for strong homeotropic anchoring at the surface of a nanoparticle (cf. System V in Table II).

where the colloidal particles are separated by $2R$, implying that the colloidal particles are in contact, and surrounded by a single halo. Increase of the density to $\rho^* = 0.294$ results in a PMF strikingly similar to that at the lowest density, with the small repulsion at $r = 14\sigma$ removed, and the barrier at $r = 11\sigma$ significantly enhanced.

Within the nematic phase, strong fluid layering is evidenced by the undulations in the PMF starting immediately at the order parameter wall. Two attractive minima, just below $r = 2R + 3\kappa\sigma$ and $r = 2(R + \kappa\sigma)$ are observed before strong repulsion sets in upon overlap of the two layers. Each minimum is several $k_B T$ in depth, with a minimum of $\approx 5k_B T$ prevailing at $r = 12.5\sigma$. This state is important for the counterpoint it provides to continuum calculations (e.g., Ref. 22), which predict much deeper contact attractions for nanoparticles when the defect regions overlap. Comparison between these and our PMF minima should be somewhat tempered by the fact that the theoretical calculations consider primarily a single orientation of the nematic director to the particle separation; a quantity which is naturally averaged over here. Some of these states are repulsive due to such misalignment, which reduces the effective depth of the minimum. It should similarly be noted that in our case, the discrete Gay-Berne particles require a large energy to break from the surface, strongly limiting the allowed separations relative to the continuum case.

IV. DISCUSSION AND CONCLUSIONS

These simulations demonstrate that nontrivial interactions occur between nanoparticles in mesogenic solvents when nematic wetting layers are present. Due to the finite size of particles in our study, all simulations which allow solvent to be evicted from the surface experience a deep minimum corresponding to depletion attraction. When strong anchorings are considered, this possibility is mitigated, and a strongly layered PMF appears near the surfaces of the particles. Notably, however, weak homeotropic anchorings experience a local minimum in the isotropic phase PMFs corresponding to a sharing of their wetting layers. This attraction disappears upon transition to the nematic phase. Of the cases considered, only the case of strong homeotropic anchoring obtains deep local minima ($\approx 5k_B T$) within the isotropic phase. Representative conformations (cf. Fig. 9) show that attractions to arise through very different configurations. Figure 9(a) depicts the sharing of planar-anchored layers by two nanoparticles. Though these layers do not exhibit strong local nematic ordering, the sharing nonetheless allows these particles to strongly attract. By contrast, the strong homeotropic anchoring, which shows attraction in the nematic phase, gives rise to a defect structure reminiscent of the “three-ring” defect observed in continuum simulations of infinite-anchoring nanoparticles.²¹

In agreement with recent simulations¹³ which failed to obtain gelation in simulations of nematic suspensions of particles with planar anchoring, we find that strong planar anchoring results in net repulsive interactions in the nematic phase. Interestingly, in these systems a net attraction is observed for isotropic solvents near the nematic transition. The resulting

FIG. 9. Representative attractive configurations for two systems. Mesogens are colored by local order parameter to elucidate how structure influences the potential of mean force. (a) A configuration contributing to the attractive well for $\rho^* = 0.294$ in the isotropic phase with anchoring parameters II in Table II. Pure red particles have local ordering $S > 0.3$, while pure blue particles are disordered. While mesogens near each particle are disordered, planar-anchored mesogens are seen to be shared by adjacent nanoparticles. (b) A configuration from the attractive well for $\rho^* = 0.321$ in the nematic phase and anchoring parameters V in Table II. Pure red particles have ordering $S > 0.5$ while pure blue particles are disordered. A three-ring structure²¹ is visible within the disordered particles.

interactions have strength $\approx 2k_B T$, which likely depends on the planar anchoring strength, possibly strong enough to support physical gelation. Sufficiently strong homeotropic anchoring is also able to create minima deep enough to support gelation ($\approx 5k_B T$), for nanocolloids in both the isotropic and nematic phases.

We conclude from these simulations that strong anchoring is able to produce gelation within the isotropic phase. As PMFs are concentration-dependent, the weak minima observed within simulations with homeotropic anchoring may be enough to facilitate physical gelation at high enough colloid concentrations. To test this further, we performed simulations of nanocolloids which have been loaded into mesogenic solvent following the procedure outlined in Sec. II, where the solvent has been pre-prepared into the equilibrium isotropic or nematic state. We then add 100 nanoparticles with $\sigma = 4\sigma_0$, resulting in a loading fraction of 12.4%. Our goal is

FIG. 10. Mean-square displacement of nanoparticles at 12.4% loading fraction. Anchoring conditions refer to Table II.

to determine if these samples will gel. Four cases are studied, corresponding strong homeotropic or planar anchorings (cf. Figs. 6 and 8). To determine the onset of kinetic arrest, we track a running approximation of the mean-square displacement, $\langle (x(t) - x(0))^2 \rangle$ where the brackets denote an average over all particles. This is plotted in Fig. 10. It can be seen that after 10 000 t_0 , each of these interactions has exited the initial linear regime of the mean-square displacement (MSD). Note that the planar anchored particles are much more mobile than the homeotropic particles. This is primarily due to strong haloing by mesogens (cf. Fig. 9(b)). To see if the particles have then formed a gel, we apply the following strain protocol to the output simulations. First, the simulation is run for 10 t_0 under constant volume conditions. A uniaxial strain is then applied in the x direction, extending the box by 5% over a time $10t_0$ under constant volume restriction. Finally, the box is allowed to equilibrate to its new shape. We monitor the residual stress $\Delta\sigma_i = P_0 - P_i$, where P_0 is the hydrostatic pressure of the suspension, and P_i is the pressure on a plane normal to direction i . A gel will be expected to hold residual stress while a fluid will not. It is seen from Fig. 11 that after an initial jump in stress, a planar-anchored system retains residual stress indicative of gelation in the isotropic phase but not in the nematic phase. A similar response is seen for homeotropic anchoring within the isotropic phase.

It should be noted that we have chosen a short-ranged ordering field for these simulations. This naturally leads to a very small wetting layer thickness, ξ_W , which in turn limits the strength of the interactions. Though this quantity is tunable by temperature⁴² in the vicinity of the IN transition, here it is a static parameter set by the anchoring potential. Were this ordering field to penetrate further into the fluid, more nuanced interactions with many structural features are likely. This will be a subject of future investigation. Further, the systems we have investigated here have nanoparticles with radii far below those studied experimentally.⁴⁶ With the advent of cryo-EM⁶⁸ and liquid-cell TEM⁶⁹ techniques, the local ordering of nanoparticles in such a gel phase, and even the local nematic defect structure may be probed. Liquid-cell TEM in particular is able to investigate such structures without freezing, enabling direct imaging of the nanoparticle–LC composites as they form, potentially enabling direct measurement

FIG. 11. Residual strain during the time-dependent relaxation protocol described in the text. Clockwise from top left: isotropic fluid with strong planar anchoring, nematic fluid with strong planar anchoring, nematic fluid with strong homeotropic anchoring, and isotropic fluid with strong homeotropic anchoring. Roman numerals refer to anchoring conditions in Table II. Colors: σ_{xx} , red; σ_{yy} , green; σ_{zz} , blue.

of the PMF. Currently, however, connection of our simulations and those examined in theoretical investigations (e.g., Refs. 35 and 36) requires scaling to larger systems as computational speed improves and further enhanced sampling techniques for slowly diffusing systems are developed.

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