

Self-organization of tip-functionalized elongated colloidal particles

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Weakly attractive interactions between the tips of rodlike colloidal particles affect their liquid-crystal phase behavior due to a subtle interplay between enthalpy and entropy. Here we employ molecular dynamics simulations on semiflexible, repulsive bead-spring chains where one of the two end beads attract each other. We calculate the phase diagram as a function of both the volume fraction of the chains and the strength of the attractive potential. We identify a large number of phases that include isotropic, nematic, smectic-*A*, smectic-*B*, and crystalline states. For tip attraction energies lower than the thermal energy, our results are qualitatively consistent with experimental findings: We find that an increase of the attraction strength shifts the nematic to smectic-*A* phase transition to lower volume fractions, with only minor effect on the stability of the other phases. For sufficiently strong tip attraction, the nematic phase disappears completely, in addition leading to the destabilization of the isotropic phase. In order to better understand the underlying physics of these phenomena, we also investigate the clustering of the particles at their attractive tips and the effective molecular field experienced by the particles in the smectic-*A* phase. Based on these results, we argue that the clustering of the tips only affects the phase stability if lamellar structures (“micelles”) are formed. We find that an increase of the attraction strength increases the degree of order in the layered phases. Interestingly, we also find evidence for the existence of an antiferroelectric smectic-*A* phase transition induced by the interaction between the tips. A simple Maier-Saupe-McMillan model confirms our findings.

DOI: [10.1103/PhysRevE.100.042702](https://doi.org/10.1103/PhysRevE.100.042702)**I. INTRODUCTION**

Elongated colloidal particles form additional phases under conditions in between those where the well-known isotropic (disordered) and crystalline (ordered) phases are found [1–3]. The particles are invariably aligned but have no or only partial (short-range or quasi-long-range) positional order in these phases and, for this reason, are called liquid-crystalline phases. The phase transitions are driven primarily by entropy, as theoretical, simulation, and experimental studies have shown [4–11]. More recently, the use of selective surface functionalization of elongated colloidal particles has opened up an interesting novel path of investigation, allowing us to modify the self-assembled liquid-crystalline phases and/or to manipulate their stabilities. For example, such particles have been explored in the synthesis of functional materials including nanowires and batteries [12–15] and in the investigation of specific structure formation such as multipods, tubes, and bottle brushes [16–19]. Nevertheless, studies concerning how a relatively weak and highly local surface modification affects the phase sequences for a wide range of concentrations, as well as particles characteristics such as aspect ratio and bending flexibility, remain scarce.

A good example of functionalized elongated colloids is the recent work by Repula *et al.* using filamentous M13 virus particles [20], which measure 1 μm in length and 7 nm in width and which have persistence length of about 3 μm . In their experiments, the M13 virus has its terminal (P3) protein modified, allowing for the attachment of red dye molecules to one of the tips of these polar particles. The procedure results in a controllable, attractive, single-end local interaction in what was previously a purely repulsive rod. From previous work, we know that the complete phase sequence of suspensions of such viruses comprises isotropic (*I*), nematic (*N*), smectic-*A* (*Sm-A*), smectic-*B* (*Sm-B*), columnar (*Col*), and crystalline (*Cry*) phases [10]. Interestingly, the surface modification seems to affect only one of various phase transitions: The nematic-smectic-*A* phase transition is influenced by the number of red-dye molecules grafted to the virus tip, stabilizing the latter phase. For the purpose of understanding the reason for this, we investigate how a weakly attractive tip modifies the liquid crystalline behavior of repulsive, semiflexible rodlike particles using computer simulations.

In this paper, we present the calculated phase diagram of such particles as a function of both the concentration and the attraction strength between tips, demarcating two regimes. In the first regime, in which the strength of the tip-tip interaction corresponds to energies lower than or comparable to the thermal energy, our results are qualitatively consistent with the experimental findings [20]. In the second regime, corresponding

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to slightly stronger attractive energies, we find interesting effects including the complete suppression of the nematic phase and the destabilization of the isotropic phase. Additionally, we address in this paper several other topics regarding the microstructure of the phases, such as: (1) qualitative and quantitative aspects of the supramolecular aggregation due to the presence of the attractive tips in the various phases, (2) the response of the interlayer distance and the molecular field for the various concentrations and attraction strengths between the tips in the smectic and crystalline phases, and (3) evidence for the existence of an antiferroelectric smectic-A phase induced by the interaction between the ends.

Related to the antiferroelectric smectic-A phase, note that the bilayer structure is antiferroelectric in one dimension. In two dimensions or, in other words, within a smectic layer, the structure is ferroelectric. We make an analogy with ferroelectricity instead of ferromagnetism for historical reasons. The term was previously employed in the literature of liquid crystals, referring to compounds that form bilayer structures in the smectic-A phase [21]. The term (anti)ferromagnetism is usually restricted to magnetic phenomena, while (anti)ferroelectricity is more liberally used, referring to various types of polar phenomena [22]. The existence of an antiferroelectric phase of end-functionalized hard rods with double periodicity was anticipated long ago by Jackson and coworkers by means of density-functional theoretical calculations [23]. We also present a simple model based on the Maier-Saupe-McMillan theory that describes the phase transition within the smectic-A phase and that qualitatively explains our simulation results.

The remainder of this paper is structured as follows. We describe the methods and model particle employed in our computer simulations as well as the data analysis procedure in Sec. II. In Secs. III and IV, we present the results followed by a discussion. These sections are devoted to the phase behavior and the microstructure of the phases. In Section V, we present our most important conclusions. Finally, in the Appendix, we present our Maier-Saupe-McMillan theory for end-functionalized, perfectly parallel rods.

II. METHODS AND ANALYSIS

A. Model particles

We model the semiflexible rodlike particles as the bead-spring chains of n overlapping beads of diameter D and mass m . Consecutive pairs of beads interact via a harmonic potential $U_r = \kappa_r(r - D/2)^2/2$, which means that the beads overlap by a half diameter. Here r is the bond length and κ_r is the harmonic bond stretch constant that we fix to a reasonably high value of $100 k_B T/D^2$, where $k_B T$ denotes the thermal energy with k_B Boltzmann's constant and T the absolute temperature. Consecutive bonds between beads interact via a harmonic bending potential, $U_\theta = \kappa_\theta(\theta - \pi)^2/2$, where θ is the angle between two consecutive bonds and κ_θ the harmonic bend constant. Except for the first and second neighbors within a chain, the interactions between the beads are given by a steeply repulsive potential for which we use the Lennard-Jones potential, truncated at its minimum and shifted to zero, i.e., $U_R = 4\epsilon_0[(R/D)^{-12} - (R/D)^{-6}] + \epsilon_0$ if $R \leq 2^{1/6}D$ and

$U_R = 0$ if $R > 2^{1/6}D$, where R is the center-to-center distance between the beads and ϵ_0 the strength of the interaction, which is kept constant and equal to $1 k_B T$. The single-end attractive interaction is modelled using a second type of bead at one of the ends of every chain, represented in red in the snapshots of our simulations (Fig. 3). These beads interact with each other via the full Lennard-Jones potential, $U_{LJ} = 4\epsilon[(R/D)^{-12} - (R/D)^{-6}]$, with various values of $\epsilon \geq 0$. Notice that because only one end of every chain is sticky, the chains are polar and lack inversion symmetry.

B. Particle characteristics

Due to the harmonic bond stretch, the contour length of the particles, L , and, consequently, their mean aspect ratio, $L/D = (n-1)\langle r \rangle/2$, where $\langle r \rangle$ is the average bond length, are slightly variable. We refer to the mean aspect ratio at very low densities, L_0/D , to characterize our particles. The actual contour length of the particles is somewhat smaller than this, in particular in the more congested phases due to the high ambient pressure that compresses the particles somewhat. See Ref. [24] for a discussion. The persistence length L_P of the particles depends on the harmonic bend constant. We have $L_P = \kappa_\theta \langle r \rangle / k_B T$, at least for an infinitely large number of beads and $\kappa_\theta \langle r \rangle^2 / k_B T \gg 1$ [25]. The value for the end-to-end distance of particles of various persistence lengths obtained in our previous simulations compares well with the value of the end-to-end distance predicted by the wormlike chain model in the isotropic phase, showing that the relation is indeed appropriate to describe the persistence length of our particles even though they are not infinitely long [24]. We quantify the particles' flexibility by the ratio of the dilute-solution contour length and the persistence length, L_0/L_P . Simulations are performed for chains of aspect ratio $L_0/D = 10.77$ and flexibility $L_0/L_P = 0.3$. The aspect ratio chosen gives us a reasonable compromise between equilibration time and particle number in simulations at high concentrations. The flexibility matches the one of the experimental model particles mentioned earlier [20]. More details are given in Sec. III. We perform preliminary simulations on somewhat shorter and stiffer chains of $L_0/D = 6.46$ and $L_0/L_P = 0.1$ (results not shown). The only impact aspect ratio seems to have is that the volume fractions at which the various phase transitions take place decreases as the aspect ratio increases, as in fact expected from previous studies [24]. The same is true for the effect of bending flexibility, which increases the volume fraction at which the various phase transitions occur. Hence, we focus our presentation in this work on results for the longer particles.

C. Molecular dynamics

We perform molecular-dynamics (MD) computer simulations using the software package LAMMPS [26]. We simulate 4608 bead-spring chains in a box in order to obtain structural properties of the tip attractive rodlike particles. Our simulations run for 20 000 time units that, in physical quantities, correspond to $\sqrt{mD^2/\epsilon_0}$. We employ time steps of 10^{-3} in these units, in other words, a total of 2×10^7 time steps. We save configurations every 2×10^5 time steps. The volume V

of the box is equilibrated for fixed temperature T and pressure P , using the Nosé-Hoover thermo- and barostat, which allows the box dimensions to adjust independently [26]. This choice is important to accommodate layered phases and obtain their undistorted interlayer distance. From the average equilibrated volume V , we calculate the volume fraction ϕ with the expression $\phi = Nv_0/V$, where v_0 is the volume of the spherocylinder whose length is equivalent to the average length of the chains at very low densities, $v_0 = \pi D^3/6 + \pi D^2 L_0/4$. That means that the actual volume fraction is slightly lower than the value we adopt to represent it. This choice is made in order to keep most of the parameters of our simulation fixed. The results we present in this paper are from expansion simulation runs starting from a crystal-like configuration, which we describe in more detail in the paragraph below. We also perform compression runs for the particles without attractive end tips for all phase transitions identified. These results are not shown. In these runs, the initial configuration is obtained from an (expansion) equilibrium configuration at a lower pressure P (or volume fraction ϕ) near the phase transition. From the compression runs, we note that the phase transitions take place at the pressure we expected from the expansion simulations. The largest disagreement in the calculated volume fraction of the resulting more condensed phase is 0.5%. For this reason, our simulations starting from the crystal-like configuration seem to be robust.

D. Initial configurations

For the expansion simulation runs, we consider diverse variations of the crystal-like initial configurations corresponding to how our polar particles are oriented. In all configurations, the particles are organized in 16 AAA stacked layers. In each layer, particles are organized in a hexagonal lattice and aligned parallel to the z direction. For this reason, if particles in our simulations have a preferential direction, which is described by the director \mathbf{n} , then this is usually approximately parallel to the z direction, $\mathbf{n} \parallel \hat{\mathbf{z}}$. In the first type of initial configuration, all attractive beads are in the upper tip of the particle. Even though our simulation time is relatively long, it is not sufficiently long to equilibrate the system at all concentrations. In other words, in the more condensed phases, we do not reach 1:1 chains up and down relative to the director. In the second type of initial configuration investigated, the attractive beads alternate between the upper and the bottom tip within the same layer. In the third type of initial configuration tested, half of the layers have the attractive groups in the upper tip and the other half have the particles' attractive bead in the bottom tip. These layers alternate in a way that this third configuration has a bilayer type of structure. The latter two initial configurations result in structures with fewer or no defects at all. Hence, in the following sections, we present the results from the simulations in which the third type of initial configuration is used.

See in Fig. 1 the schematic representation of the three initial configurations followed of a snapshot from the preliminary simulations (in which our particles have an aspect ratio $L_0/D = 6.46$ and a flexibility $L_0/L_P = 0.1$) after 20 000 000 time steps at approximately constant volume fraction

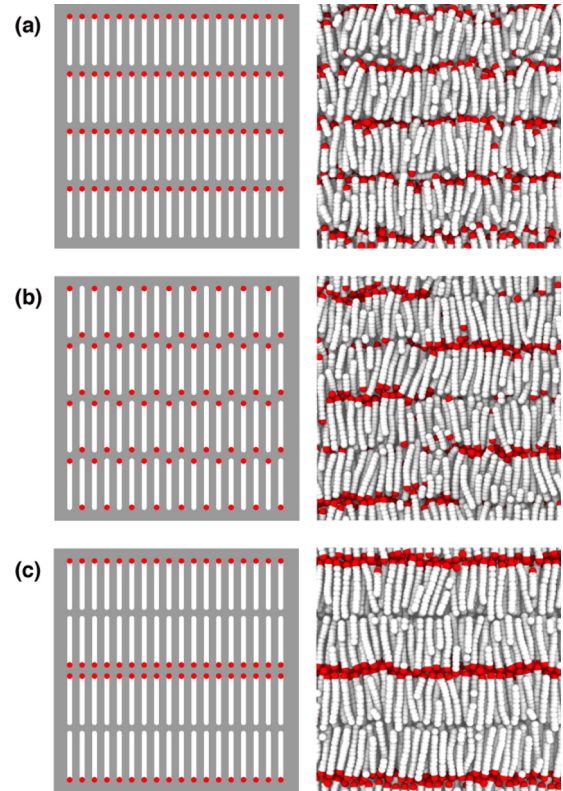


FIG. 1. Schematic representation of the initial configurations and snapshots of resulting configurations after 20 000 000 time steps of simulations starting from each of them at approximately constant volume fraction $\phi = 0.52$ (at a fixed pressure $1.7 \epsilon/D^3$) for the attraction strength of $0.6 k_B T$. In the initial configuration in (a), all particles have the same orientations, in (b), particles alternate orientation within the same layer, and in (c), all particles have the same orientation within the layer, but the orientation alternate from consecutive layers.

$\phi = 0.52$ (at a fixed pressure $1.7 \epsilon/D^3$) for the attraction strength of $0.6 k_B T$.

E. Phase classification

Our equilibrium configurations are classified using order parameters (OPs) and correlation functions. The liquid-crystalline phases we first distinguish from the isotropic phase by quantifying the degree of alignment of the particles through the usual nematic OP. A second OP quantifies the organization of the particles in layers. If layers are not formed, then we have either a nematic or a columnar phase. If layers are formed, then we have either smectic or crystalline phases. A third OP quantifies the hexagonal bond order. This procedure allows us to distinguish between nematic and columnar and between the smectic-A and the smectic-B and crystal phases. This final classification is possible by studying the correlation of the bond order (measuring two-dimensional hexagonal order) and the pair correlation function (probing radial in-plane positional order). Using this procedure, we are able to distinguish between all known phases of the fd virus suspensions, mentioned in Sec. I. Our analysis procedure is similar to the one employed in our previous work to which we refer for

details [24]. We also identify two distinct smectic and crystalline phases due to the attraction between the functionalized tips. The procedure to distinguish between them we describe below in the paragraph dealing with the antiferroelectric phase transition.

F. Aggregation statistics

Further analysis is required in order to study the structure of supramolecular assemblies in all phases, in particular in the layered phases where the spacing is expected to be influenced by (i) the attraction strength between tip beads and (ii) the concentration of the particles. We quantify the aggregation of the particles by focusing on cluster sizes. By *cluster* we refer to groups of attractive tip beads that are spatially close or connected by a bead satisfying this criterion. We arbitrarily choose a radius r_c . The first choice for r_c is $1.24D$. This value corresponds to the second root of a parabola, whose minimum is at the minimum of the Lennard-Jones potential and the first root coincides with the root of this potential. If pairs of attractive tip bead are closer than this distance, then we consider them as belonging to the same group. Note that not all beads in a group need to be closer than r_c , as some can be connected indirectly via other attractive beads, as represented in the inset of Fig. 4, in Sec. IV.

G. Antiferroelectric phases

Due to the polarity of our molecules, we identify two types of organization in layered phases: one in which the attractive tip beads are present in roughly equal numbers in every interlayer spacing and another in which the attractive tip beads are mostly present in every other interlayer spacing, creating a bilayer structure with double periodicity of that of the layers. In order to pinpoint the transition between these two states within our phase diagram, we project the particle orientations on a vector along the director. We define the orientation vector of the particles connecting the repulsive end bead to the attractive end bead. The two extreme situations are as follows: (1) the rods are in a bilayer type of configuration and, as a result, all particles within a layer are either parallel or antiparallel to a vector along the director; and (2) the ratio between parallel and antiparallel particles to the same vector within a layer is 1:1. For these cases, if the fractions of particles in a particular orientation in even and odd layers are respectively $f = 0$ and 0.5 , then the antiferroelectric order parameter is defined as $\delta = 1 - 2f$. We choose the value $\delta = 0.5$ as a criterion to classify the phases as the usual smectic-A ($\delta < 0.5$) or the antiferroelectric smectic-A₂ ($\delta \geq 0.5$). The same procedure is applicable to the smectic-B and crystalline phases, whose corresponding antiferroelectric phases are denoted smectic-B₂ and crystalline₂ phases. From snapshots of our simulations, we find that even at the lowest attraction strength investigated, the smectic-B and crystalline phases are antiferroelectric.

H. Layer thickness

We utilize two different procedures to calculate the interlayer distance in the layered phases. As a first procedure, we take the value that maximizes the Fourier component of the normalized distribution of center of masses along the

director [27]. This does not differentiate between the layers regarding the fraction of particles pointing up. Because there are two types of smectic-A phase, we expect that the interlayer distance is different if in their interface there are mostly attractive or repulsive tips. In order to measure this difference in the bilayered phase, we plot the histogram of counts of the center of mass for each (arbitrary) interval of positions along the director. In the layered phases, the distribution of the centers of mass of the particles along the director is peaked around the centers of the layers. Hence, we fit a Gaussian function to each counting of the center of mass divided by the maximum count, $g_j(z) = e^{-b_j(z-a_j)^2}$, where e is the usual Euler constant. The parameter b_j is related to the standard deviation s of the Gaussian function by $b_j = 1/2s^2$ and describes how well ordered the layers are. The center of the Gaussian distribution a_j corresponds to the position of the j th layer along the director. The distance between two consecutive layers is then calculated as $\lambda_j = a_{j+1} - a_j$. Beyond the antiferroelectric transition, the values of λ_j with odd j correspond to the distance between layers in which there are more attractive tips than tails facing each other. For this reason, the average value λ_{odd} is expected to be lower than λ_{even} beyond the antiferroelectric transition; λ_{even} is then the average over the values λ_j with even j and over the equilibrium configurations for a given pressure.

I. Smectic ordering potential

The smectic ordering potential $\Delta U(z)$ describes the molecular field experienced by each individual particle in the smectic-A phase. It is obtained from the distribution of the particles' centers of mass along the z direction, which corresponds approximately to the director \mathbf{n} , $\rho(z)$. More specifically, the relation $\rho(z) \propto e^{-\Delta U(z)/k_B T}$ holds by virtue of assuming a Boltzmann distribution. We fit this relation to the simulation data to extract $\Delta U(z)$. From the smectic ordering potential, we compare between various attraction strengths and volume fractions how well defined the layers are and how difficult it is for a particle to hop from layer to layer. We quantify it by measuring the difference between the highest and lowest values of the smectic ordering potential ΔU , which defines the height of the smectic ordering potential $h_{\Delta U}$, for several values of the attraction strength and volume fraction. We also estimate the width of the smectic ordering potential $w_{\Delta U}$ by calculating the full width at half maximum of $\rho(z)$, using the standard deviation s of the Gaussian function described in the previous paragraph, giving $w_{\Delta U} = 2\sqrt{2 \ln 2} s$.

III. PHASE BEHAVIOR

We focus attention on the phase behavior of semiflexible rodlike particles that have an aspect ratio of $L_0/D = 10.77$ and a flexibility of $L_0/L_p = 0.3$. The flexibility of our model particles matches that of the M13 virus investigated in Ref. [20] albeit that the aspect ratio of our particles is considerably shorter by a factor of 10. Actually, the effective aspect ratio of the viruses, accounting for the electric double layer of the M13 particles, is about 3 times our aspect ratio. We choose to simulate shorter particles, because it enables us to investigate them for a wide range of concentrations,

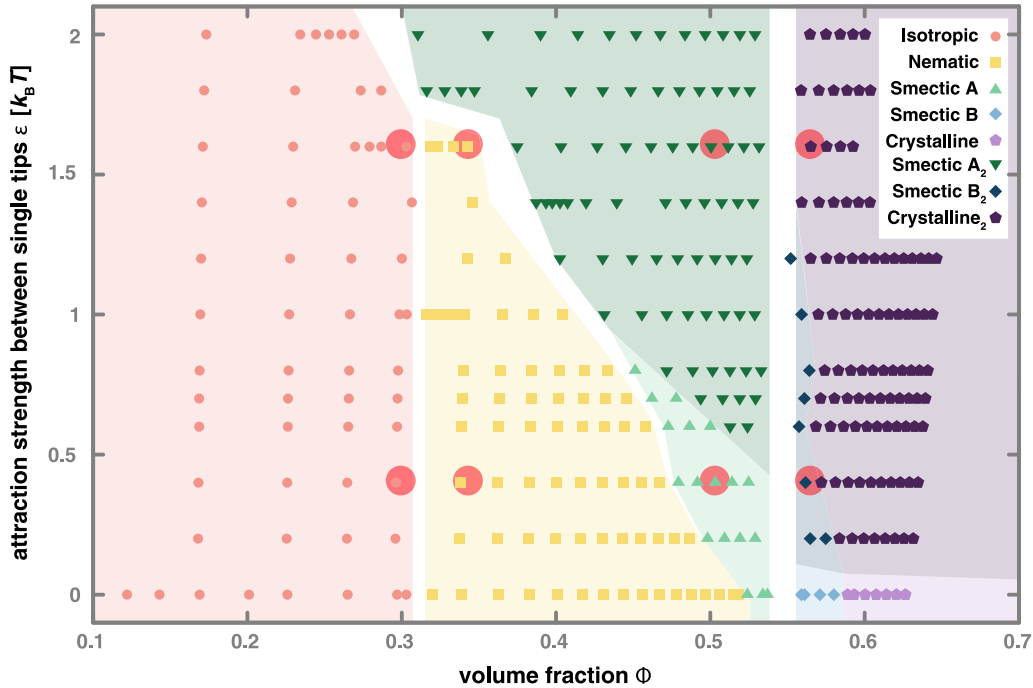


FIG. 2. Calculated phase diagram of repulsive, rodlike particles that have a single attractive tip as a function of the attraction strength between the end tips (in units of thermal energy $k_B T$) and the volume fraction ϕ . The particles have a base aspect ratio $L_0/D = 10.77$ and flexibility of $L/L_p = 0.3$ (see the main text.) The following phases are identified: isotropic (orange circle), nematic (yellow square), smectic-A (green up-triangle), smectic-A₂ (dark green down-triangle), smectic-B (blue diamond), smectic-B₂ (dark blue diamond), crystalline (purple pentagon), and crystalline₂ (dark purple pentagon). Snapshots of the data points highlighted by red circles in the phase diagram are presented in Fig. 3.

keeping the same number of particles in our simulation box and the total simulation time. In general, as the aspect ratio of the particles is reduced, the phase transitions of their suspensions are shifted to larger volume fractions because the excluded volume interaction is less anisotropic. Still, both experimental and simulation particle models support the same phases except for the columnar phase, which has not yet been observed in particle-based simulations involving monodisperse particles [24,28–30]. Therefore, we are able to compare them in what is our main interest in this paper: the increase of the stability of the smectic-A phase at the expense of the nematic phase.

In the phase diagram presented in Fig. 2, the phase sequence at the zero attraction strength, $\epsilon = 0 k_B T$, is taken from our previous work [24]. In this case, the particles are purely repulsive and have the same total number of beads as the particles with an attractive tip. Note that, as they are not equipped with the attractive bead, these rods are not polar. For these purely repulsive particles, the phase sequence consists of the following phases from lower to higher volume fractions: isotropic, nematic, smectic-A, smectic-B, and crystalline phases. From these simulations, we find that the isotropic-to-nematic and the smectic-A-to-smectic-B phase transitions seem to be of the first order. The smectic B-to-crystalline phase transition appears to be continuous, while the nematic-to-smectic-A phase transition is either continuous or weakly first order. In the recent work of Milchev *et al.*, in which very large-scale simulations of semiflexible particles are performed, the latter transition is continuous [31]. For the model particles described under *Methods*, we

vary the depth of the attraction well ϵ of the Lennard-Jones potential between the beads representing the functionalized tips of the viruses, that is, the *attraction strength*, from 0.2 to $2 k_B T$. The calculated volume fraction is within the range of approximately 0.1 to 0.7. In order to obtain more resolution in volume fraction near the isotropic-nematic transition, we perform additional simulations for the attraction strengths 1 and $1.6 k_B T$ near the transition. We do likewise for the nematic-smectic-A and isotropic-smectic-A phase transitions for the attraction strengths 1.4 and $1.8 k_B T$. We separate our discussion of the phase diagram in the next two paragraphs, related to the low- and a medium-energy regime of the single-end, attractive interaction on account of the qualitative difference in behavior.

A. Lower attraction strengths

For values of the attraction strength up to about $1 k_B T$, our simulations show that there is no significant change in the isotropic-to-nematic phase transition. Comparing the sequences at 0 and $1 k_B T$, which is the one with more resolution in volume fraction in this regime of attraction strengths, we find that the largest and lowest volume fractions in which these phases are stable in our simulations (corresponding to the coexistence concentrations) coincide. For this reason, the isotropic-to-nematic phase transition remains first order. We find that the nematic phase is destabilized in favor of the smectic-A phase and that this phase transition becomes more strongly first order as the strength of the attraction interaction is increased. These findings are consistent with the recent

experimental observations on aqueous suspensions of M13 virus [20]. Our most remarkable finding is an antiferroelectric phase transition within the smectic- A phase. We identify the new smectic- A_2 phase, characterized by a bilayer type structure, in our phase diagram at $0.4 k_B T$ and higher attraction strengths, depending on the density. Section IV provides more details about the antiferroelectric transition, which in our simulations is continuous. There are also antiferroelectric smectic- B and crystalline phases. In fact, even at the lowest attraction strength investigated, we find only the antiferroelectric smectic- B_2 and crystalline $_2$ phases, suggesting that only tiny interaction energies are required to stabilize these. We did not attempt to pinpoint at what low value of ϵ the transition happens for these phases. As for the other phase transitions, we find that there is no significant change in the smectic- A –or smectic- A_2 –to–smectic- B_2 phase transition. Furthermore, the smectic- B_2 phase destabilizes with increasing value of ϵ and the crystalline $_2$ phase becomes more stable at lower volume fractions. We understand that the suppression of the smectic- B_2 phase is due to the increased ordering of particles due to the sticky end groups, as we shall see below when discussing the changes in the microstructure of the phases with increasing attraction between the tips. Note that, despite the distinct polarity caused by a single sticky end, this fundamentally does not allow for macroscopically polar phases as the sticky ends attract each other.

B. Higher attraction strengths

In order to investigate the effect of larger attraction energies between the end groups, we performed simulations for attraction strengths up to $2 k_B T$. The phase sequence at $1.2 k_B T$ follows the trends described in the previous paragraph. For this reason, the coexistence concentrations (volume fractions) of the nematic and smectic- A_2 phases are even lower and the difference between them (the phase gap) becomes larger. For stronger attraction, the smectic- B_2 disappears, and as a result the smectic- A_2 –to–smectic- B_2 phase transition is replaced by a smectic- A_2 –to–crystalline $_2$ transition. This transition seems to be independent of the attraction strength and the phases have similar coexistence volume fractions as the transition at lower values of the attraction strength. Between attraction strengths 1.6 and $1.8 k_B T$, we find that the nematic phase is completely suppressed in favor of the smectic- A_2 , thus also affecting the stability of the isotropic phase. Therefore, the phase sequence at the highest attraction strengths 1.8 and $2 k_B T$ consist of only three phases: isotropic, smectic- A_2 , and crystalline $_2$. From these results, we find that the isotropic phase may also be further destabilized with increasing attraction strength between the tips. A similar transition between an isotropic and a smectic- A phase with additional double periodicity was found in simulations of hinged rods for a model of gapped DNA complexes [32]. These authors dubbed this phase the Sm- fA , where the f stands for folded because the rods are folded at the hinge, creating this additional double periodicity of the position of the hinges in the structure. From the simulations at increased resolution, we are able to conclude that the isotropic-nematic phase gap in volume fraction is about 0.02 for the attraction strength of $1 k_B T$ and only slightly larger for $1.6 k_B T$, corresponding to approximately

0.03 . Therefore, the order of this phase transition does not seem to be strongly affected by the attractive end aggregation. On the other hand, the nematic-smectic- A_2 , as previously discussed, and isotropic-smectic- A phase transitions become more strongly first order with an increase of the attraction strength, as we find from the more detailed sequences at the attraction strengths of 1.4 and $1.8 k_B T$.

The phase diagram presented here compares reasonably well with the phase diagram obtained from the numerical solving of our simple Maier-Saupe-McMillan model for end-functionalized, perfectly parallel rods [Fig. 11(b)]. See the Appendix for a discussion. Next, we discuss in more detail the microscopic structure of the various phases.

IV. MICROSTRUCTURE OF THE PHASES

In this section, we present the most salient features of the microstructure of the various phases, focusing in particular on those of the smectic- A and smectic- A_2 phases in order to better understand what drives the antiferroelectric phase transition. First, we discuss the qualitative and quantitative changes in the aggregation of the particles with attractive tips. For this purpose, we investigate snapshots as well as the aggregation statistics of the particles in the various phases. Second, we discuss the behavior of the interlayer distance for the smectic and crystalline phases, as well as their antiferroelectric version based on results from the two different analysis procedures described in Sec. II. Next, we provide more details about the order of the antiferroelectric phase transition, presenting the order parameter used for the classification of the smectic- A and smectic- A_2 phases. Finally, we analyze the stability of the smectic- A and smectic- A_2 at a constant volume fraction, using the smectic ordering potential for various attraction strengths. For the different phases, we identify the following features.

A. Clustering of particles

In the next paragraphs, we describe how the aggregation of elongated particles is influenced by the strength of the attractive tips in the various phases. The snapshots in Fig. 3 represent the aggregation patterns at approximately constant volume fraction ϕ in the isotropic phase at $\phi \sim 0.30$ (a), nematic phase at $\phi \sim 0.38$ (b), smectic- A and smectic- A_2 phases at $\phi \sim 0.51$ (c), and smectic- B and crystal phases at $\phi \sim 0.56$ (d). Left to right, each pair of snapshots shows examples of configurations of particles with attraction strengths of 0.4 and $1.6 k_B T$. The snapshots show that the aggregation pattern of the tips is clearly distinct, depending on the attraction strength for particles in the same phase and at the same volume fraction, as we describe in detail in the paragraph below.

From our phase diagram in Fig. 2, we find that the isotropic-to-nematic transition is only affected for $\epsilon \geq 1.6 k_B T$. At this attraction strength, lamellar, disk-, or inverted-micelle-like structures are formed. These two different aggregation patterns are represented in the snapshots on the right in Figs. 3(a) and 3(b). In Fig. 3(a), we find that, overall, the particles have random orientations, as expected for the isotropic phase. The particles aggregated in lamellar structures have similar orientation but the structures themselves have diverse orientations. In Fig. 3(b), at attraction strength

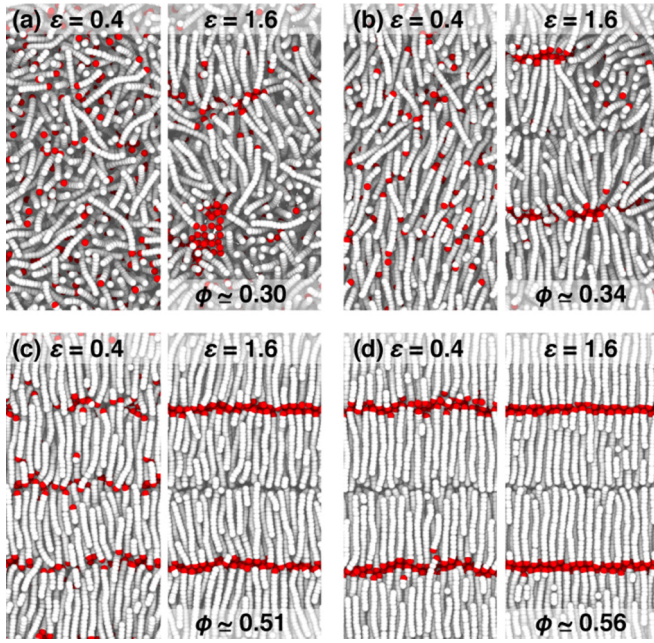


FIG. 3. Snapshots of the simulations at approximately constant volume fraction ϕ in the (a) isotropic phase at $\phi \approx 0.30$, (b) nematic phase at $\phi \approx 0.38$, (c) smectic-A and smectic-A₂ phases at $\phi \approx 0.51$, and (d) smectic-B (left) and crystal phases (right) at $\phi \approx 0.56$ obtained. From left to right, a pair of snapshots for each value of the volume fraction is given for attraction strengths of 0.4 and 1.6 in units of $k_B T$. The corresponding data points are highlighted by red circles in the phase diagram in Fig. 2.

$1.6 k_B T$ (right), we note that the alignment of the particles in the nematic phase results in a structure that resembles a highly disordered smectic phase. In view of that, we conclude that the formation of such lamellar structures must be the reason that there is a suppression of the nematic phase in favor of the smectic phase. In the snapshots of Fig. 3(c), we compare how particles are organized along the director in the smectic-A (left) and the smectic-A₂ (right) phases at the same volume fraction. We find that the layers become more well defined with increasing attraction strength. This is confirmed comparing the snapshots of Fig. 3(d) for the smectic-B₂ and crystalline₂ phases. The attraction between the tips increases the degree of order of the particles, reducing the stability range of the smectic-B₂ phase in favor of the crystalline phase.

We compare these patterns with the corresponding aggregation statistics as a function of the volume fraction in Fig. 4, where we present [Fig. 4(a)] the average tip aggregation number for various attraction strengths and [Fig. 4(b)] the fraction of particles in monomers, dimers, and trimers or larger aggregates for an attraction strength of $0.2 k_B T$. Figure 4(a) shows, as expected, that the average aggregation number increases with increasing attraction strength and with increasing concentration due to mass action [33]. The microstructure therefore changes even in the isotropic phase, although, surprisingly, the isotropic-nematic phase transition is not affected at all. As we infer from the inset in Fig. 4, the tip clustering is weak at attraction strengths up to $1 k_B T$ in both the isotropic and the nematic phases. For these phases and attraction strengths, the aggregation numbers remain modest

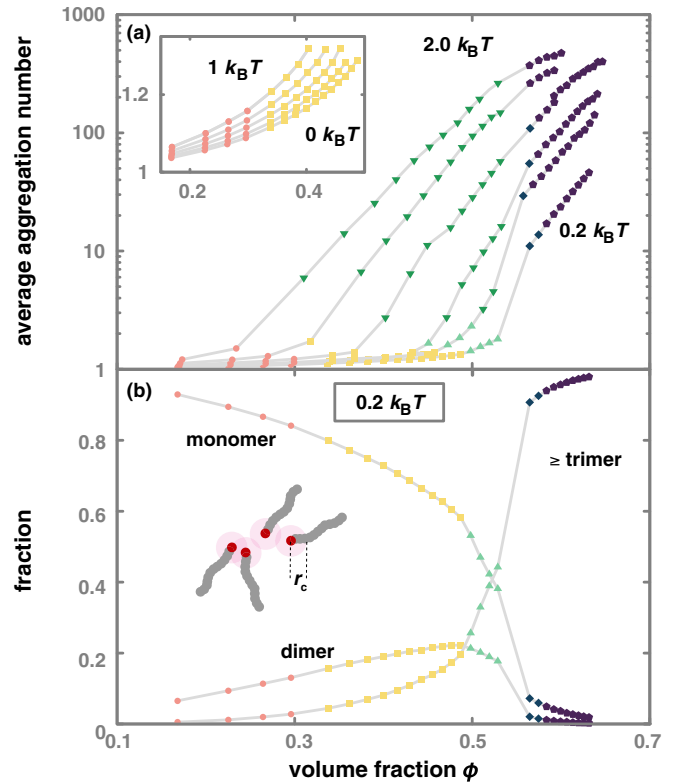


FIG. 4. (a) Average aggregate size for various attraction strengths between the end groups as a function of the volume fraction of particles. Attraction strengths 0.2, 0.6, 0.8, 1.2, 1.6, and 2.0 in units of $k_B T$ from right to left. The inset is an enlarged view of the graph for lower volume fractions for attractive strength equally spaced between 0 and $1 k_B T$. (b) Fraction of monomers, dimers, trimers, or larger aggregates, which are connected via the attractive ends for attraction strength 0.2 in units of $k_B T$. The particles have aspect ratio $L_0/D = 10.77$ and a flexibility of $L_0/L_p = 0.3$. The following phases are identified: isotropic (orange circle), nematic (yellow square), smectic-A (green up-triangle), smectic-A₂ (dark green down-triangle), smectic-B₂ (dark blue diamond), and crystalline₂ (dark purple pentagon).

even though growth is stronger than a linear increase with the volume fraction. Actually, in these phases the average aggregation number is not larger than 1.3, which means that the tips are mostly monomers. Figure 4(b) confirms this: In both the isotropic and the nematic phases, the fraction of monomers and dimers predominate. The fraction of trimers or larger aggregates surpasses the fraction of dimers only in the smectic-A phase and then the fraction of monomers in the smectic-B₂ phase. This indicates that larger aggregates are formed due to the inherent structure of the phase rather than due to the attraction strength alone. Indeed, part of the clustering is due to the change in the contact value of the pair distribution function with increasing pressure [34]. For this reason, there is aggregation of tips even for $\epsilon = 0 k_B T$ and the aggregation becomes much more prominent in the smectic and crystalline phases, and their antiferroelectric versions on account of the strongly increased pressures. Note the abrupt increase in size in going from the isotropic or nematic to the smectic-A₂ phase for stronger attractions and from smectic-A

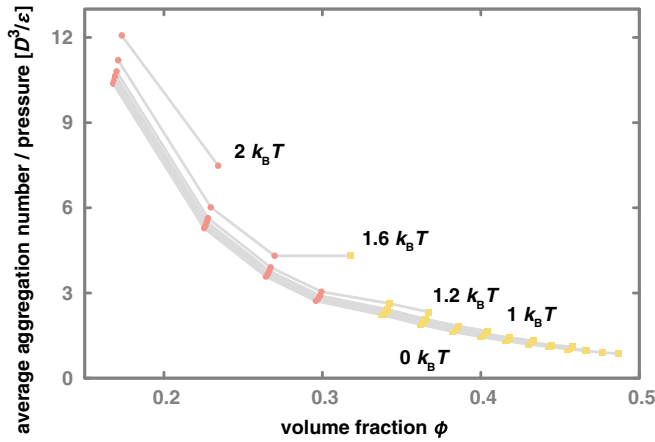


FIG. 5. Average aggregation number for the attraction strengths between 0 and 2 in units of $k_B T$ divided by pressure and presented as a function of the volume fraction ϕ in the isotropic (orange circle) and nematic (yellow square) phases. The particles have a base aspect ratio $L_0/D = 10.77$ and flexibility of $L/L_p = 0.3$.

or smectic- A_2 to smectic- B_2 for weaker attractions in Fig. 4(a). This in all likelihood is connected with the transition appearing strongly first order.

Figure 5 corresponds to another version of the inset of Fig. 4(a). In this figure, we present the average aggregation number divided by the pressure P in the isotropic and nematic phases for the attraction strengths between 0 and $2 k_B T$, presented as a function of the volume fraction ϕ . The overlapping of the curves for the attraction strengths between 0 and $1 k_B T$ indicates that, at this interval of attraction energies, the aggregation of the attractive tips is mainly due to the mass action [34].

B. Interlayer distance

The interlayer distance λ corresponds to the average distance between the center of masses of consecutive layers. This quantity comprises the average layer size added to the average interlayer gap, as represented in the inset of Fig. 6 and depends on the characteristics and interactions of the particles. As described under *Methods*, we apply two different analysis procedures to our data in order to investigate the interlayer distance. We refer to the results relative to the standard procedure as the *averaged* interlayer distance and to the results relative to the second procedure as the *differentiated* interlayer distance. The main difference is that in the second procedure we differentiate between odd and even layer numbers. In Fig. 6, we present the averaged interlayer distance λ relative to the average particle length $L + D$ as a function of the volume fraction ϕ for attraction strengths between the end groups ranging in strength from 0 to $2 k_B T$. In Fig. 7, we present the values of the differentiated interlayer distance for even λ_{even} and odd λ_{odd} over the particle length $L + D$ as a function of the volume fraction ϕ for attraction strengths 0.2, 0.6, and $1.0 k_B T$. Note that the length L is not the bare length but the actual, measured value, somewhat compressed by the ambient pressure.

In Fig. 6, we find that the scaled interlayer distance $\lambda/(L + D)$ exhibits a rich behavior depending on the attrac-

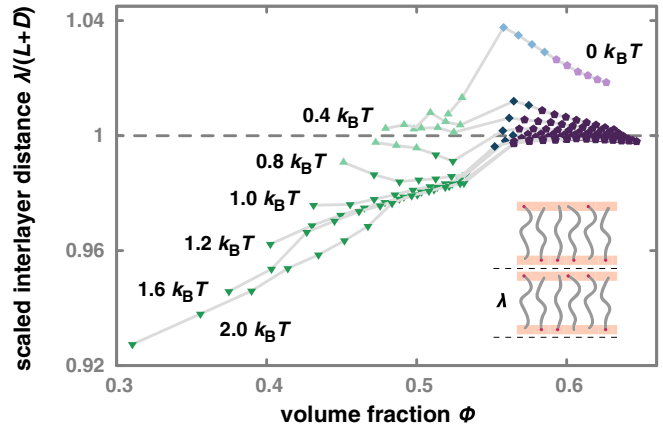


FIG. 6. Scaled interlayer distance $\lambda/(L + D)$ of repulsive, rod-like particles with a single attractive tip as a function of the volume fraction ϕ for attraction strengths between the end groups ranging from 0 to 2 in units of $k_B T$ from top to bottom in the smectic-A (green up-triangle), smectic- A_2 (dark green down-triangle), smectic-B (blue diamond), smectic- B_2 (dark blue diamond), crystalline (purple pentagon), and crystalline $_2$ (dark purple pentagon) phases. Particles have aspect ratio $L_0/D = 10.77$ and a flexibility of $L_0/L_p = 0.3$. The inset is an illustration representing the interlayer distance λ .

tion strength between the tips and on the state of aggregation. In the smectic-A phase and at attraction strengths larger than or equal to $1 k_B T$, the scaled interlayer distance increases with the volume fraction. Note that these values are smaller than unity, which means that the layers slightly interdigitate. This interpenetration lowers the interaction energy because it allows for a larger surface contact between the tips, which consist of an exposed attractive hemispherical cap. Between 0.8 and $0.6 k_B T$, the interlayer distance seems to decrease with increasing volume fraction. Interestingly, it is for these

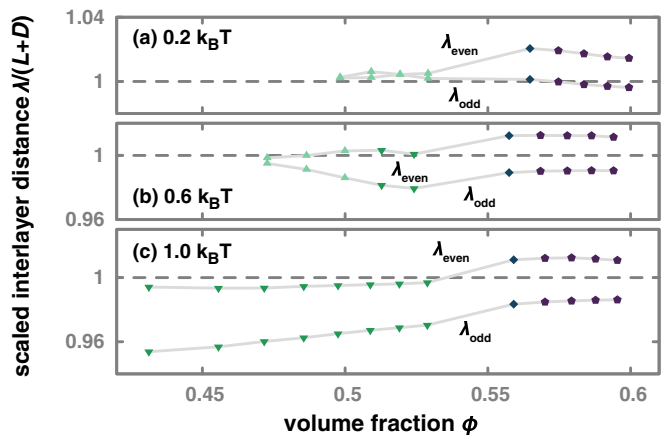


FIG. 7. Average interlayer distance relative to the average rod length $\lambda_{\text{odd}}/(L + D)$ for odd and $\lambda_{\text{even}}/(L + D)$ for even interlayer distances of repulsive, rodlike particles that have an attractive tip in the smectic-A (green up-triangle), smectic- A_2 (dark green down-triangle), smectic- B_2 (dark blue diamond), and crystalline $_2$ (dark purple pentagon) phases for attraction strengths of (a) 0.2, (b) 0.6, and (c) 1.0 in units of $k_B T$. Particles have aspect ratio $L_0/D = 10.77$ and flexibility of $L/L_p = 0.3$.

strengths that we identify both the smectic- A and the smectic- A_2 phase. For lower attraction strengths, the scaled interlayer distance is slightly larger than unity, indicating that, in this case, layers are nearly touching each other. Nevertheless, the dependence on the volume fraction is not obvious. Overall, the scaled interlayer distance seems to decrease with increasing attraction strength between tips. This effect is unambiguous if we consider volume fractions lower than 0.45. In other words, at a fixed volume fraction, layers interpenetrate more as the attraction strength between tips increases. As a result, the inlayer density is expected to be smaller. In fact, in a previous paper, where we investigate the semi-flexible repulsive rods, we find similar behavior [24]. In the smectic- B and the crystalline phases or the smectic- B_2 and the crystalline $_2$ phases, we note that the scaled interlayer distance decreases with volume fraction and that the value converges to unity with increasing volume fraction for all attraction strengths.

Figure 6 clarifies several features of our system but hides the distinction between layers present in the antiferroelectric phases. In Fig. 7, which presents results from the differentiated analysis, there is the distinction between odd and even interlayers at three values of the attraction strength. At the first value of $0.2 k_B T$, represented in (a), we find that the interlayer distance is approximately the same for even and odd interlayers in the smectic- A phase. As expected, their values are also approximately equivalent to the averaged layer thickness, once the layers are nearly indistinct in this phase. Nevertheless, in the smectic- B_2 and crystalline $_2$ phases, the values for the even and odd interlayer distance, which respectively contain the smaller and larger fraction of attractive tips, are distinct. The former is larger than unity and the latter is approximately unity. These values slightly decrease with the volume fraction. In Fig. 7(b), the results are for the attraction strength of $0.6 k_B T$. In the smectic- A phase, we find that for that case the values of the odd and even interlayer distances are approximately equal only at the lowest volume fraction and that they become distinct as the volume fraction increases. Notice that the even interlayer distances are larger than the odd ones, because even though the antiferroelectric order parameter δ is different from zero, it is smaller than $1/2$ and hence the phase is not classified as smectic- A_2 . The even interlayer distance is approximately constant and equal to unity, while the odd interlayer distance becomes smaller, meaning that the layers in these interfaces are also interpenetrating. In the smectic- A_2 phase, the even interlayer distance follows the same trend as in the smectic- A phase, while the odd interlayer is slight smaller but the dependence on volume fraction is not clear due to the lack of data points available in this phase. In the smectic- B_2 and crystalline $_2$ phases, it seems that even and odd interlayer distances do not depend on the concentration. Their values are slightly above and below unity, respectively. We find the same for an attraction strength of $1.6 k_B T$, as we see in Fig. 7(c). For the smectic- A_2 phase, we find that the values are rather different and that, while the trend for even interlayer distance remains as described before, the odd interlayer distance, which is smaller than unity, tends to slightly increase with increasing volume fraction. This effect is probably due to the lower in-layer density of particles

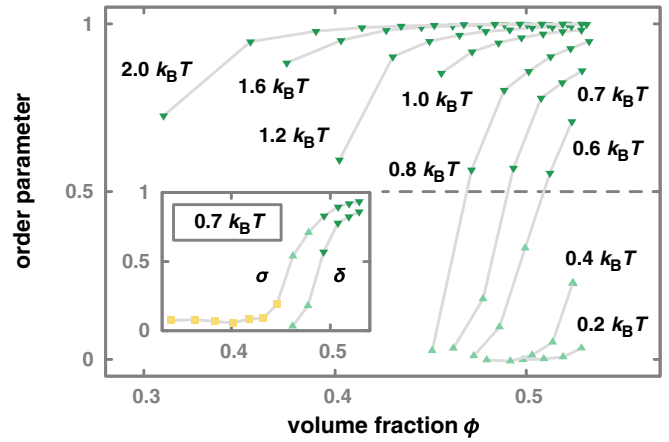


FIG. 8. Antiferroelectric order parameter δ of repulsive, rodlike particles that have a single attractive tip as a function of volume fraction ϕ for various values of the attraction strength between the attractive tips. In the inset we compare the antiferroelectric δ and smectic σ order parameters for the attraction strength of 0.7 in units of $k_B T$. Particles have aspect ratio $L_0/D = 10.77$ and flexibility of $L_0/L_P = 0.3$. The following phases are identified: nematic (yellow square), smectic- A (green up-triangle), and smectic- A_2 (dark green down-triangle) phases.

at lower volume fractions, which offers more space for the particles to interpenetrate.

C. Antiferroelectric phase transition

The antiferroelectric phase transition in the phase diagram is linked with the polarity of our single-ended attractive elongated particles. We identify this phase transition using the antiferroelectric order parameter δ , defined in Sec. II, and presented in Fig. 8 as a function of the volume fraction ϕ for various values of the attraction strength. Its value continuously increases with increasing volume fraction, which indicates a second-order phase transition. As previously mentioned, we are not able to pinpoint the antiferroelectric phase transition in the smectic- B and crystalline phases: We find the smectic- B_2 and crystalline $_2$ even at the lowest attraction strength investigated ($0.2 k_B T$). In the inset, the antiferroelectric order parameter δ is represented together with the smectic σ order parameter as a function of concentration for attraction strength $0.7 k_B T$. The smectic order parameter itself does not provide a clear indication of the presence of an antiferroelectric transition although it could be masked by our limited resolution in the volume fraction ϕ . For a comparison with our simple Maier-Saupe-McMillan model, where we do see much more enhanced smectic ordering beyond the transition [Fig. 11(a)], we refer to the Appendix and to Fig. 9, which is another version of the inset of Figure 8. In the figure, we compare the smectic order parameter σ as a function of $\Delta\phi/\phi_{N-Sm}$, where $\Delta\phi$ is the difference between the volume fraction and the volume fraction at the nematic-to-smectic- A (for $\epsilon = 0 k_B T$) or-smectic- A_2 phase (for $\epsilon = 0.7 k_B T$) transition, $\Delta\phi = \phi - \phi_{N-Sm}$. The volume fraction ϕ_{N-Sm} at the transition is estimated by the average between the highest and lowest values of the volume fraction at which, respectively, the nematic

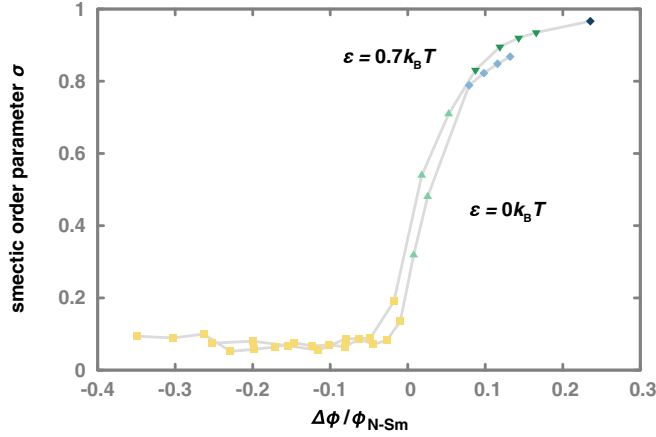


FIG. 9. Smectic order parameter σ of repulsive, rodlike particles that have a single attractive tip as a function of $\Delta\phi/\phi_{N-Sm}$, where $\Delta\phi$ is the difference between the volume fraction and the volume fraction at the nematic-to-smectic-A (for $\epsilon = 0$) or smectic-A₂ phase (for $\epsilon = 0.7 k_B T$) transition, $\Delta\phi = \phi - \phi_{N-Sm}$, for attraction strengths of 0 and $0.7 k_B T$. Particles have aspect ratio $L_0/D = 10.77$ and flexibility of $L_0/L_P = 0.3$. The following phases are identified: nematic (yellow square), smectic-A (green up-triangle), smectic-A₂ (dark green down-triangle), smectic-B (blue diamond), and smectic-B₂ (dark blue diamond) phases.

and smectic-A or smectic-A₂ phases are stable. We find that the smectic order parameter σ is smaller at smaller attraction strength from the comparison of the values of ϵ between 0 and $0.7 k_B T$. Therefore, this result shows that the degree of order increases due to the attraction between single tips in the layered phases.

D. Smectic ordering potential

The smectic ordering potential $\Delta U(z)$ represents the molecular field that a particle experiences from the other particles within a smectic layer. We calculate it for our simulations in the smectic-A phase around the antiferroelectric phase transition, as represented in the top inset of Fig. 10. From the inset, we find that both the height and the width changes as we increase the attraction strength at a constant volume fraction of $\phi = 0.52$: The potential barrier increases and becomes narrower around the center of the layer $z/L = 0.5$. In other words, the smectic layers become increasingly ordered, as we also see from the snapshots in Fig. 3(c). The smectic ordering potential seems to show more noise at higher attraction strengths, in particular in between the layers. This, in all likelihood, is due to the poor statistics: Once the particle centers of masses are concentrated around the center of the layer fewer particles venture out between the layers. From Fig. 10, we find that the height of the smectic ordering potential linearly increases with the attraction strength at the volume fraction of $\phi = 0.52$, and the trend does not seem to be changed crossing the antiferroelectric phase transition. The same is true if the volume fraction is increased at constant attraction strength, as it is shown in the top inset of Fig. 10. Therefore, our particles are more strongly attached to a layered structure and, on top of that, the layer itself

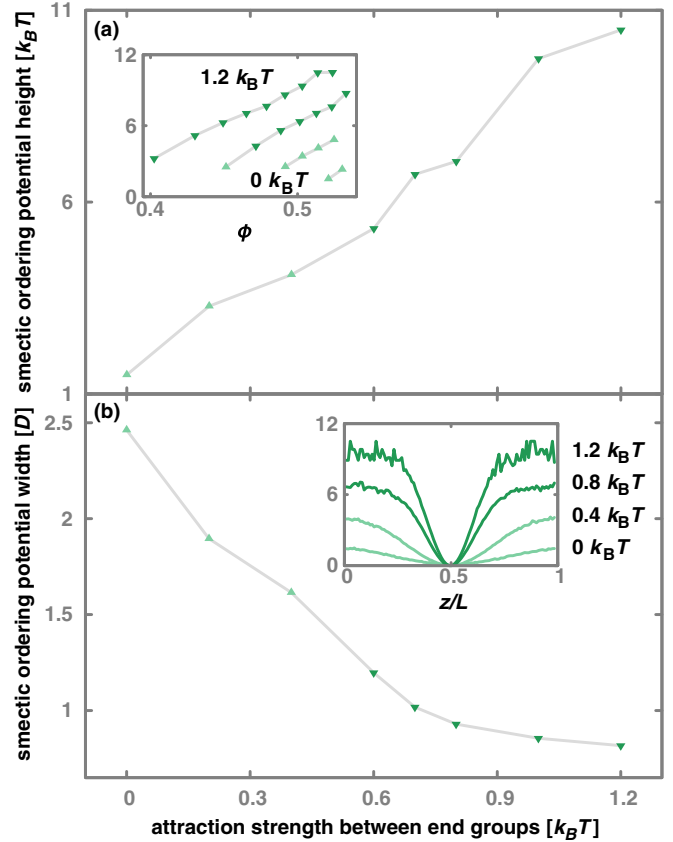


FIG. 10. Smectic ordering potential of repulsive, rodlike particles with a single attractive tip. Particles have an aspect ratio of $L_0/D = 10.77$ and a flexibility of $L_0/L_P = 0.3$. (a) Height of the smectic ordering potential of repulsive as a function of the attraction strength between tips in the smectic-A (green up-triangle) or smectic-A₂ (dark green down-triangle) phases at a volume fraction of $\phi \cong 0.52$. In the inset, there is the same height of the smectic ordering potential of repulsive as a function of the volume fraction for attraction strengths 0, 0.4, 0.8, and 1.2 in units $k_B T$. (b) Width of the smectic ordering potential of repulsive as a function of the attraction strength between tips in units of $k_B T$. In the inset, the smectic ordering potential $\Delta U(z)$ is presented as a function of the position along the director, normalized by the particle length z/L . The increase of the attraction strength drives the stabilization of the smectic-A and smectic-A₂ phases.

is more strongly confined due to the small amplitude in the fluctuations of the particle positions around the average. This molecular field of particles in the smectic phase as well as the smectic and antiferroelectric order parameters, presented in the previous paragraph, are also reasonably well described by our simple Maier-Saupe-McMillan model (see Figs. 13 and 14 in the Appendix).

V. DISCUSSION AND CONCLUSION

The aim of the present work is to study by means of molecular dynamics simulations the influence that attractive interaction between one of the two ends of a collection of otherwise mutually repulsive, elongated particles have on their phase behavior, using computer simulations. Our work

shows that their phase behavior, and the structure of the various liquid-crystalline phases, are strongly affected even by relatively weak interaction strengths on the order of the thermal energy. The phase behavior has two striking features: (1) the formation of bilayered antiferroelectric phases and (2) the large increase of stability of smectic- A at the expense of the nematic phase, and even at the expense of the isotropic phase as we increase the attraction strength between the tips beyond about $1.6 k_B T$. The key factor is the interplay between the interaction energy, polarity of the particles, and the phase microstructure. The analysis of the microstructure reveals that the stability of the isotropic and nematic phases is affected by the aggregation of the tips, only if the particles align in response to the local increase in concentration. In the layered phases, the organization of the particles with the attractive tips results in more strongly ordered microstructures even at very weak attraction energies.

Our results concerning the shift of the nematic-to-smectic- A phase transition to lower volume fractions, which also seems to become more strongly first order with an increase of the attraction strength, are supported by experimental evidence. Despite the fact that the difference in the aspect ratio between simulated and experimental particles prevents us to make a quantitative comparison, we are able to qualitatively compare the smectic ordering potential of the experimental and computational model particles. We find for both of them larger values of the height and smaller values of the width as the attraction strength between tips increases. As expected, because the experimental model particles are larger in aspect ratio, their smectic potential height is also larger, due to the increase of stability of the smectic- A phase with increasing aspect ratio [35]. In our theory (Appendix), the shift of the nematic-to-smectic- A phase transition is independent of the volume fraction. Nevertheless, the shift to lower volume fractions is captured if the nematic-to-smectic- A_2 phase transition is considered. The height and width of the effective smectic ordering potential from our Maier-Saupe-McMillan theory does not emulate the smectic ordering potential from our simulations. This might be due to our choice of representing it as a cosine function instead of a Gaussian function.

In spite of the obvious limitations, our study does contribute to the understanding of how selective surface functionalization of colloidal liquid crystals affects their self-organization by providing a systematic study of the stability and structure of these phases for a wide range of both volume fractions and attraction strengths. We show that incorporating a single (enthalpic) functionalized end in elongated colloidal particles gives rise to an even more complex and rich phase behavior than for the purely repulsive ones. In the light of this, we suggest that agreement between purely repulsive models and experiment cannot be expected because residual attractive interactions, local or global, strongly influence the phase behavior.

ACKNOWLEDGMENTS

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implementing the numerical integration of the equations presented in the Appendix.

APPENDIX: THE ANTIFERROELECTRIC PHASE TRANSITION WITHIN A MAIER-SAUPE-MCMILLAN TYPE THEORY

Here we describe a simplified model for the antiferroelectric phase transition for N perfectly parallel, rodlike particles, equipped with a single tip attractive interaction. These particles are aligned along the z axis, forming the nematic phase if they are uniformly distributed or smectic phases if their positions are periodically distributed along the z axis. The periodicity in the smectic phases is d , corresponding to the spacing between the layers. The single tip attraction is the key element for the existence of the smectic- A_2 phase. In this bilayered phase, the distribution of the attractive tip has the periodicity $2d$.

Our description is inspired by Maier-Saupe-McMillan theory [36,37]. We write the Helmholtz free energy F in one layer as the sum of the Gibbs entropy, proportional to the position density distribution along the director of both the elongated particles $p(z)$ and the attractive tips $f(z)$, and energy terms proportional to the molecular field or smectic ordering potential, $\Delta U_{\text{Sm}A}(z)$, and the interaction energy between attractive tips, $\Delta U_{\text{Sm}A_2}(z)$,

$$\frac{\beta F}{N} = \int_{-\frac{d}{2}}^{+\frac{d}{2}} dz \left[p(z) \ln p(z) + \frac{1}{2} p(z) \beta \Delta U_{\text{Sm}A}(z) \right] + \int_{-\frac{d}{2}}^{+\frac{d}{2}} dz \left[f(z) \ln f(z) + \frac{1}{2} f(z) \beta \Delta U_{\text{Sm}A_2}(z) \right].$$

The factor $1/2$ in the energy terms corrects for double counting; the distribution functions $f(z)$ and $p(z)$ are properly normalized.

The energy term $\beta \Delta U_{\text{Sm}A}(z)$ drives the nematic-smectic- A phase transition and it is expected to be proportional to the volume fraction $\phi \in [0, 1]$ and the smectic ordering parameter σ , so

$$\beta \Delta U_{\text{Sm}A}(z) = -\phi \gamma \sigma \cos\left(\frac{2\pi z}{d}\right), \quad (\text{A1})$$

where γ is an adjustable parameter and the cosine describes the periodic molecular field (of periodicity d). The smectic ordering parameter mentioned previously in this work is given by

$$\sigma = \int_{-\frac{d}{2}}^{+\frac{d}{2}} dz p(z) \cos\left(\frac{2\pi z}{d}\right). \quad (\text{A2})$$

Note that (A1) is temperature invariant: It represents the hard-core nature of the interactions. The energy term $\beta \Delta U_{\text{Sm}A_2}(z)$ drives the antiferroelectric transition and it should arguably be also proportional to the volume fraction ϕ and some power of the smectic ordering parameter σ , as well as to the antiferroelectric order parameter δ itself. We put forward

$$\beta \Delta U_{\text{Sm}A_2}(z) = -\phi \sigma^2 \tilde{\epsilon} \delta \sin\left(\frac{2\pi z}{d}\right),$$

where $\tilde{\epsilon}$ is a (dimensionless) measure for the strength of the attraction between the tips and the sine function represents the periodicity $2d$ of the antiferroelectric state. There is no obvious mapping of the sticking energy of our simulations and that of our model, although we would guess that $\tilde{\epsilon} \propto \epsilon$. The antiferroelectric ordering parameter is given by

$$\delta = \int_{-\frac{d}{2}}^{+\frac{d}{2}} dz f(z) \sin\left(\frac{2\pi z}{2d}\right). \quad (\text{A3})$$

In equilibrium, the free energy must be functionally minimized, $\delta(\beta F/N)/\delta p = \lambda$ and $\delta(\beta F/N)/\delta f = \mu$, accounting for the normalization conditions

$$\int_{-\frac{d}{2}}^{+\frac{d}{2}} dz p(z) = \int_{-\frac{d}{2}}^{+\frac{d}{2}} dz f(z) = 1,$$

which require us to introduce the Lagrange multipliers λ and μ .

Making use of the normalization of $p(z)$, we find that

$$p(z) = \frac{\exp\left[\sigma\phi(\gamma + \tilde{\epsilon}\delta^2)\cos\left(\frac{2\pi z}{d}\right)\right]}{\int_{-\frac{d}{2}}^{+\frac{d}{2}} dz \exp\left[\sigma\phi(\gamma + \tilde{\epsilon}\delta^2)\cos\left(\frac{2\pi z}{d}\right)\right]}. \quad (\text{A4})$$

Note that $\tilde{\epsilon}$ is an energy scaled to the thermal energy and hence temperature dependent. From thermodynamics, we have $\tilde{\epsilon}(T) = \tilde{\epsilon}(T_0) - \tilde{h}(T_0)(T - T_0)/T_0$, with \tilde{h} a dimensionless enthalpy and T_0 a reference temperature. For hydrophobic interactions $\tilde{h} < 0$, implying that the molecular field increases in strength with increasing temperature.

We employ the same procedure for $f(z)$, and find

$$f(z) = \frac{\exp\left[\delta\phi\sigma^2\tilde{\epsilon}\sin\left(\frac{2\pi z}{2d}\right)\right]}{\int_{-\frac{d}{2}}^{+\frac{d}{2}} dz \exp\left[\delta\phi\sigma^2\tilde{\epsilon}\sin\left(\frac{2\pi z}{2d}\right)\right]}. \quad (\text{A5})$$

We linearize the equations for the smectic and the antiferroelectric order parameters, given by Eqs. (A2) and (A3), in which we substitute the explicit expression for the density distribution of both the elongated particles $p(z)$ and the attractive tips $f(z)$, from Eqs. (A4) and (A5). From the linearization, we obtain the following expressions for the order parameters:

$$\sigma^2 = \left[\frac{4}{\phi(\gamma + \tilde{\epsilon}\delta^2)}\right] \left[\frac{1}{2} - \frac{4}{\phi(\gamma + \tilde{\epsilon}\delta^2)}\right] \quad (\text{A6})$$

and

$$\delta^2 = \left(\frac{4}{\phi\sigma^2\tilde{\epsilon}}\right) \left(\frac{1}{2} - \frac{4}{\phi\sigma^2\tilde{\epsilon}}\right). \quad (\text{A7})$$

From Eq. (A6), we find that, in order that the smectic order parameter is positive, $\sigma \geq 0$,

$$\phi(\gamma + \epsilon\delta^2) \geq 2, \quad (\text{A8})$$

and, from Eq. (A7), we find that $\delta^2 \geq 0 \Rightarrow \phi(\gamma + \tilde{\epsilon}\delta^2) \geq 2$. From these results, we have that the transitions to the smectic-A or smectic-A₂ phases are continuous.

Alternatively, we recursively solve the coupled integral equations numerically for the smectic and the antiferroelectric order parameters, using the Mathematica software. We fix the value for adjustable parameter $\gamma = 5$ in order to shift the transitions volume fractions to values close to where we find the transitions in our simulations. The initial values for the

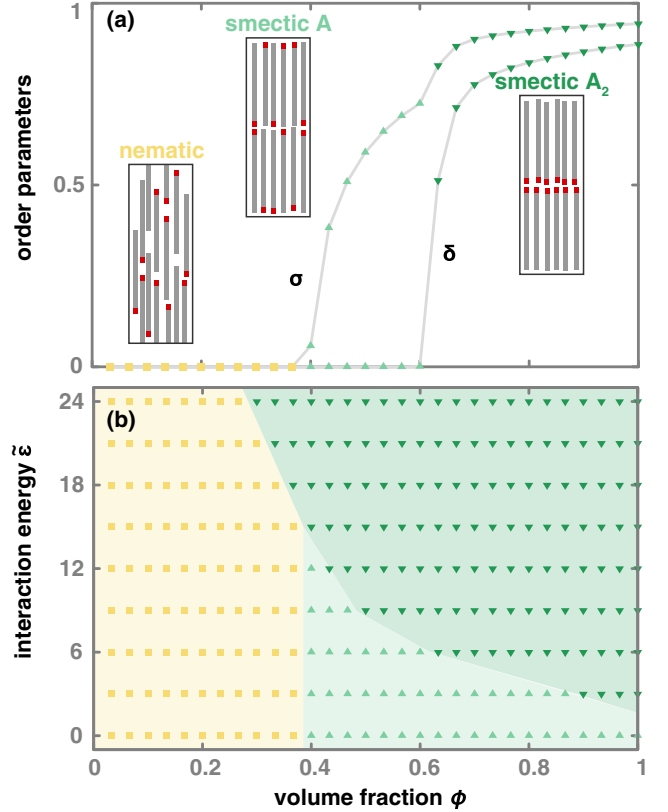


FIG. 11. Theoretical approach to describe the antiferroelectric phase transition for perfectly parallel, hard rods that have a single attractive end. Phases identified are as follows: nematic (yellow square), smectic-A (green up-triangle), and smectic-A₂ (dark green down-triangle). (a) Smectic and antiferroelectric order parameters numerically calculated for the attraction strength $\tilde{\epsilon} = 6$ and the adjustable parameter $\gamma = 5$, chosen to adjust the volume fraction interval for convenient viewing. (b) Phase diagram obtained from classification based on the order parameters for the same value of the adjustable parameter $\gamma = 5$. We find that the nematic phase is destabilized in favor of the smectic-A₂ phase and that the smectic-A phase is suppressed at high-enough attraction strength $\tilde{\epsilon}$.

smectic and the antiferroelectric order parameters is chosen to be 1. From each iteration, we obtain new estimates for σ and δ that will be the input values to the next one. The volume fraction is fixed and increased from 0 to 1 in 30 steps. The sticking energy is also fixed at values between $\tilde{\epsilon} = 0$ and 24, which we increased at steps of 3 in each run of our numerical calculations. The convergence criterion is that consecutive integration results differ less than 0.001 for at least 10 iterations.

From the results obtained using the procedure described in the paragraph above, we calculate the values for the order parameters σ and δ , with which we classify the corresponding phase at the fixed set of sticking energy and volume fraction parameters. From this procedure, we obtain the phase diagram of perfectly parallel, hard rods that have a single attractive end. In Fig. 11, we present in Fig. 11(a) the smectic σ and antiferroelectric δ order parameters as a function of the volume fraction ϕ at sticking energy $\tilde{\epsilon} = 6$ (and $\gamma = 5$) and

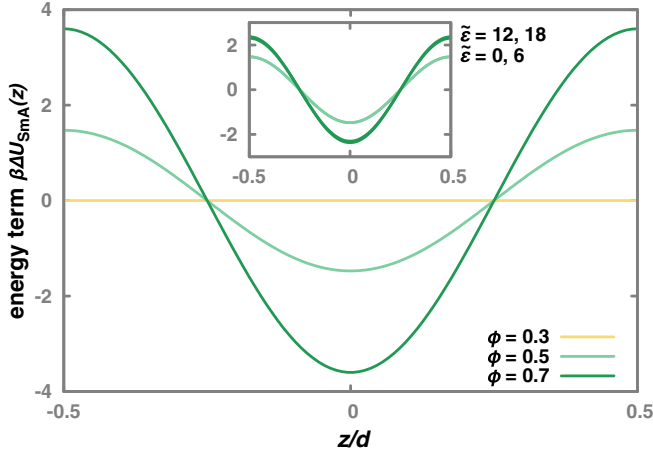


FIG. 12. Energy term $\beta\Delta U_{SmA_2}(z)$ or smectic ordering potential as a function of the position normalized by the layer thickness numerically calculated for the attraction strength $\epsilon = 6$ and the adjustable parameter $\gamma = 5$ in the nematic (at volume fraction $\phi = 0.3$), smectic-A (at $\phi = 0.5$), and smectic-A₂ (at $\phi = 0.7$) phases. In the inset, the same energy term $\beta\Delta U_{SmA_2}(z)$ calculated for the volume fraction $\phi = 0.5$ and the adjustable parameter $\gamma = 5$ in the smectic-A (at attraction strengths $\tilde{\epsilon} = 0$ and 6), and smectic-A₂ (at $\tilde{\epsilon} = 12$ and 18) phases.

in Fig. 11(b) the phase diagram obtained from classification based on these order parameters. Notice that the numerical phase diagram shows that the nematic-to-smectic-A transition is at $\phi = 0.4$, which is the value given by Eq. (A8) for $\delta = 0$ and the adopted value of $\gamma = 5$, as expected.

From Fig. 11(a), we find that, unlike the corresponding order parameters obtained from our simulations, there is a shoulder in the smectic ordering parameter at the volume fraction where the antiferroelectric phase transition occurs. It indicates that the particles become more strongly ordered along the director as the rods transition to the smectic-A₂ phase. The effect is not captured by the smectic order parameter in our simulations but this could be due to the limited resolution in our simulations. For a comparison, see the inset in Fig. 8(a). From Fig. 11(b), we find that our model captures the destabilization of the nematic phase in favor of the smectic-A₂ but the same is not true for the smectic-A. In this case, the phase transition is independent of the sticking energy. Nevertheless, the destabilization of the smectic-A in favor of the smectic-A₂ phase seems to represent what is seen in the simulations. From Fig. 12, we find that the height is approximately the same in each phase, independently of the attraction strengths between tips, unlike what we find in the simulations. The same is true for the width of the smectic ordering parameter. It is independent of both the attraction strength and the volume fraction.

The height of the effective smectic ordering potential is given by $\sigma\phi(\gamma + \tilde{\epsilon}\delta^2)$. See Eq. (A4). This quantity is represented both as a function of the volume fraction for all the attraction strengths investigated (Fig. 13) and as a function of the attraction strength for the volume fraction 0.5, in which only the smectic-A and smectic-A₂ phases are found (Fig. 14). From the comparison between Fig. 13 and the inset in Fig. 10

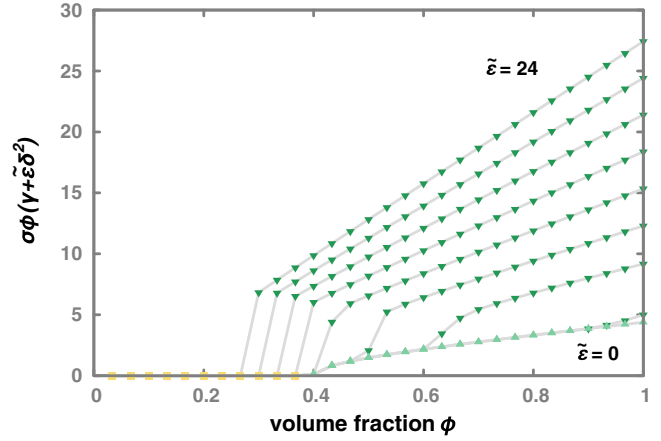


FIG. 13. Height of the effective smectic ordering potential is given by $\sigma\phi(\gamma + \tilde{\epsilon}\delta^2)$ as a function of the volume fraction for the attraction strengths $\tilde{\epsilon}$ from 0 to 24 at the interval of 3. The following phases are identified: nematic (yellow square), smectic-A (green up-triangle), and smectic-A₂ (dark green down-triangle) phases. The linear dependence of the amplitude of the smectic ordering potential with the volume fraction is also what we find in our simulations. See the inset in Fig. 10(a).

and between Fig. 14 and the Fig. 10 itself, we find that the theory emulates the linear dependence of the height of the smectic ordering potential as a function of the volume fraction and of the attraction strength except for the angular coefficient depending on the phase. The same is true for the width of the smectic ordering potential, that does not decrease as the attraction strength increases but is constant as can be seen in Fig. 12.

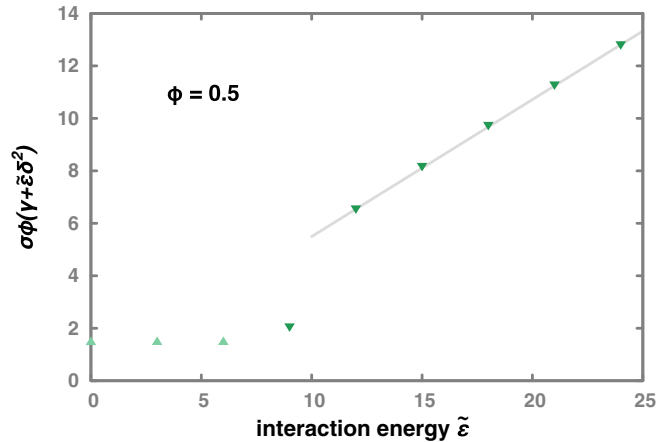


FIG. 14. Height of the effective smectic ordering potential is given by $\sigma\phi(\gamma + \tilde{\epsilon}\delta^2)$ as a function of the attraction strength at the volume fraction 0.5. The following phases are identified: smectic-A (green up-triangle) and smectic-A₂ (dark green down-triangle) phases. The linear dependence of the amplitude of the smectic ordering potential with the attraction strength is also what we find in our simulations. See Fig. 10(b).

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