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ABSTRACT
Formation of highly ordered structures usually needs to overcome a high free-energy barrier that is greatly beyond the ability of thermodynamic fluctuation such that the system would be easily trapped into a state with many defects and the annealing process of which often occurs on unreachable long time scales. Here, we report theoretically a fascinating example that active core corona particles can successfully self-assemble into a large-scaled and highly ordered stripe or trimer lattice, which is hardly achieved in a nondriven equilibrium system. Besides, such an activity-induced ordered structure shows an interesting self-healing feature of defects. In addition, there exists an optimal level of activity that most favorably enhances the formation of ordered self-assembly structures. Since core corona particles act as important units for self-assembly in real practice, we believe that our study opens a new design-strategy for highly ordered materials.

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I. INTRODUCTION

Significant advancement has been made in self-assembly of colloidal particles in recent decades. It is now possible to manipulate various types of colloidal particles to fabricate them into highly ordered functional structures, widely exploited in various fields such as in photonic, phononic, or lithographic applications. A popular choice recently for the self-assembly unit is the so-called core corona particle, which consists of an inside core (usually a metallic nanoparticle) surrounded by an ambient soft corona (e.g., polymer chains or microgels) to prevent the aggregation of cores. The interaction between two core corona particles is characterized by two repulsive length scales, related to the hard and soft repulsion, respectively. It is reported that such an interaction can result in phases with nontrivial symmetries, which include loose- and close-packed hexagonal lattice, monomer, dimer, and trimer fluids, stripe and labyrinthine phases, and honeycomb lattice, and even quasicrystals with unexpectedly high symmetry.

Note that the highly ordered equilibrium phase of the system mentioned above corresponds to the state with the lowest free energy that is thermodynamically most stable for given parameters. Such ordered structures may have great importance in material science, e.g., being used as templates for lithography nanomanufacturing that requires zero-defect patterns with even molecular level tolerance. In a real process of self-assembly in experiment, however, one generally starts from random initial conditions and the system would easily get trapped into a metastable state that is not fully ordered but with many defects. There typically exists a high free energy barrier between this metastable state and the equilibrium ordered one, which is hardly overcome by thermodynamic fluctuations such that the system would stay at the metastable state with defects for prohibitively long time scales. Therefore, how to obtain a highly ordered structure with a low fraction of defects as much as possible becomes a challenging problem in the study of self-assembly.

Recently, dynamics of self-propelled active colloids, which absorb energy from the ambient environment and push the system to a state far from equilibrium, has gained extensive research attention. A wealth of remarkable collective behaviors have been reported both experimentally and theoretically, including phase separation, active turbulence, active swarming, etc. Recently, some important works have noted the perspective of using active particles to alter the properties of colloidal aggregates. For example, Mallory and Cacciuto used a collection of triangular colloidal blocks...
with activity to achieve the self-assembly of capsidlike structures.\textsuperscript{27} In a subsequent work, they found that activity can also remarkably enhance the self-assembly process of triblock Janus colloids into the kagome lattice.\textsuperscript{28} These works suggested that it is possible to design highly ordered structures by introducing activity into the assembly unit.

Motivated by this, here in this work, we report theoretically an example that active core corona particles (ACCPs) can be successfully self-assembled into a large scaled and highly ordered structure. In the absence of activity, the extrusion between core corona particles at dense systems strongly suppresses the local arrangements; thus, the system would be trapped into metastable states with many defects as mentioned above. We find, however, if exerting an active force for each particle, the system would form a highly ordered stripe pattern or trimer lattice. In particular, such an activity-induced ordered structure owns a self-healing feature such that the system can maintain a very low defect ratio as long as the activity exists.

Besides, we also find that activity has twofold effects: while a moderate activity can facilitate the emergence of ordered structures, a strong activity could destroy the order. Therefore, it is convenient to tune the system order by simply changing the strength of activity. Our results may predict a new general routine to achieve high-ordered and self-healing structures by simply introducing active force to the self-assembly system.

This paper is organized as follows: In Sec. II, we describe the model and simulation method. Results and discussion are presented in Secs. III and IV, followed by the conclusion in Sec. V.

II. SIMULATION METHOD

We consider a simplified model of active core corona particles (ACCPs) as the assembly unit. In Fig. 1(a), a schematic diagram of a pair of ACCPs is shown. The cores with diameter $\sigma$

![Image](https://via.placeholder.com/150)

**FIG. 1.** Model setting and the characteristics of a passive system. (a) Equivalent interaction of a pair of active core corona particles. The core colored in dark green is modeled as an unpenetrable colloid that is propelled by an active force $F_a$ depicted by red arrows. Note $F_a = 0$ for (b)–(e), corresponding to a passive case. The interaction between the ambient coronas colored in light green is modeled by a simple spring in which the strength of it is $k_s$. (b) Stable spatial configuration of the system at $k_s = 200$. Note that the coronas are not drawn out for simplicity. Such a configuration consists of three typical phases, namely, stripe phase colored in green, trimer phase colored in orange, and disorder phase colored in blue. (c) Fractions of three phases $\phi_i$ ($i = S, T, D$ corresponding to stripe, trimer, and disorder, respectively) over time. (d) Equilibrium phase diagram. The phase boundary between the stripe phase and trimer phase is at $k_s = 650$ approximately. (e) Stable values of the fractions $\phi_i$ as a function of $k_s$.\textsuperscript{153}
the unpenetrable colloidal spheres described by Weeks-Chandler-Andersen (WCA)-potential:

\[ U_{\text{core}}(r_{ij}) = \begin{cases} 4\epsilon \left[ \left( \frac{r_{ij}}{\sigma} \right)^{12} - \left( \frac{r_{ij}}{\sigma} \right)^{6} + \frac{1}{4} \right] & r_{ij} < \sqrt{2}\sigma, \\ 0 & r_{ij} \geq \sqrt{2}\sigma, \end{cases} \]  

(1)

where \( r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| \) denotes the distance between two cores \( i \) and \( j \) (with the position vectors given by \( \mathbf{r}_i \) and \( \mathbf{r}_j \), respectively), and \( \epsilon \) represents the strength of WCA potential. As to ambient corona, it is shown that the repulsive force between two packed DNA-capped nanoparticles is proportional to the deformation (namely, the decrease in interparticle distance \( r_{ij} \)) proved to be the essential entropy-elastic property of polymers.\(^\text{15}\) Similar behavior can be found at a relatively larger scale, where microgels forming a corona around the microspheres can induce a soft-repulsive interaction between microspheres.\(^\text{15}\) Based on these experimental results, we model the corona interaction as a spring potential,

\[ U_{\text{corona}}(r_{ij}) = \begin{cases} \frac{1}{2}k_{c}(r_{ij} - r_c)^2 & r_{ij} < r_c, \\ 0 & r_{ij} \geq r_c, \end{cases} \]  

(2)

where \( r_c \) and \( k_{c} \) are the cutoff distance and strength of the spring potential, respectively. The equivalent interaction as a function of the distance between two ACCPs is depicted by the curve in Fig. 1(a), which consists of a soft-repulsion part in the long-distance range between coronas and a strong-repulsion part in the short-distance range between cores. Additionally, each core of ACCP is propelled by an active force \( F_a \) [shown by the red arrows in Fig. 1(a)] with an orientation undergoing random Brownian rotation.

The dynamics of ACCPs are described by the following overdamped Langevin equations:\(^\text{18}\)

\[ \dot{\mathbf{r}}_i = D_{i}\beta [F_i + \mathbf{n}_i F_a] + \sqrt{2D_i} \xi_i(t), \]  

(3)

\[ \dot{\theta}_i = \sqrt{2D_{\theta}} \eta_i(t), \]  

(4)

where \( F_i = -\sum_{j \neq i} \nabla_{\mathbf{r}_j} [U_{\text{core}}(r_{ij}) + U_{\text{corona}}(r_{ij})] \), \( \xi_i(t) \) denotes independent Gaussian white noise with zero means and unit variances, i.e., \( \langle \xi_i(t) \rangle = 0, \langle \xi_j(t) \xi_j(t') \rangle = \delta_{ij}\delta_{tt'} \), where \( \mathbf{1} \) is a unit tensor. \( F_a \) represents the strength of active force with orientation specified by the unit vector \( \mathbf{n}_i = (\cos \theta_i, \sin \theta_i) \), and \( \beta = \frac{1}{k_{\text{B}}T} \). \( D_{i} \) and \( D_{\theta} \) are translational and rotational diffusion constants, respectively, which in the low-Reynolds-number regime are related by \( D_{\theta} = \frac{D_{i}}{2\pi}. \) \( \eta_i \) are also Gaussian white noise variables as \( \xi_i \).

All simulations are performed in a square box with a 1000\(\sigma\) edge length with periodic boundary conditions. Reduced units are used in the simulations by setting \( \sigma = 1, k_{\text{B}}T = 0.1, \) and \( \tau = \frac{\sigma^2}{\epsilon} = 1. \) The system contains 4096 ACCPs, corresponding to a number density \( c \approx 0.41. \) For spring potential, \( r_c \) is set to 3.0\(\sigma\), and \( k_{c} \) is a free parameter. For WCA potential, \( \epsilon \) is \( k_{\text{B}}T. \) A stochastic Euler algorithm is employed to simulate such a dynamic equation with a maximum time step \( \Delta t = 10^{-4}\tau. \) All the reported data, if not otherwise specified, are obtained after averaging over 20 independent runs.

### III. RESULTS

#### A. Passive case

We first consider the passive case with \( F_a = 0. \) The strength of spring potential \( k_c \) is fixed to be 200 if not otherwise stated. Figure 1(b) shows the stationary pattern of the system after a long enough time, starting from a random initial condition. Note that the coronas are not drawn out for simplicity. Typically, there exist three kinds of local structure phases, i.e., stripe phase (green), trimer phase (orange), and disorder phase (blue). To identify which phase a particle belongs to, we can evaluate the angle \( \theta \) between the vectors \( \mathbf{r}_i \) and \( \mathbf{r}_j \) for each particle. As can be seen from Fig. 1(b), a large portion of the pattern is in ordered stripe and trimer phases. In Fig. 1(c), the fractions of \( \theta = S, T, D \) corresponding to stripe, trimer, and disorder phases, respectively, of each phase as functions of time \( t \) are presented, starting from a disordered state with \( \phi_D = 0.8. \) Clearly, the system relaxes very fast to the stationary state wherein the values of \( \phi \) reach stable values, say, \( \phi_S \approx 0.5, \phi_T \approx 0.1, \) and \( \phi_D \approx 0.4. \) Such a mixed state with the coexistence of stripe, trimer, and disorder phases is very stable (as can be seen from the time dependencies of \( \phi_i \)) and we have not observed any obvious changes to the configuration after a very long simulation time. That means thermal fluctuations in such a crowded system play an insignificant role to the dynamic process, in consistent with the previous experimental observations.\(^\text{15,31}\)

One should note that the mixed state shown in Fig. 1(b) is actually a metastable state of the system, rather than the equilibrium state with the lowest free energy. To get an equilibrium phase diagram for the present system, we follow the procedure used in previous studies\(^\text{15-24}\) that the system is initially heating up to a dimensionless temperature \( k_{\text{B}}T = 40.0 \) (here as an indicator of temperature) and keeps this high temperature for long enough time to make sure no obvious order emerged. Afterwards, the system is carefully cooled down with a constant cooling rate \( \Delta k_{\text{B}}T = 0.1 \) for per \( 0.1 \times 10^5 \) steps until reaching \( k_{\text{B}}T = 0.1. \) As the system cools down, particles rearrange and self-assemble into preferred low-temperature states. The equilibrium phase diagram in terms of \( k_c \) of the system is shown in Fig. 1(d). As one can see, the system shows two distinct equilibrium phases, namely, stripe and trimer, with the variation of control parameter \( k_c \) and the phase boundary is at \( k_c \approx 650. \) Therefore, the most stable state of the system with the lowest free energy for \( k_c = 200 \) should be an ordered stripe phase rather than the mixed one in Fig. 1(b). The reason that one observes a mixed-phase state that is metastable rather than the equilibrium stripe phase is that there might be a rather high free energy barrier between them, and the attraction basin of the metastable one is much larger than that of the equilibrium one. Starting from a random initial condition, it is highly probable that the system will get trapped into the local minimum of the free energy landscape corresponding to the metastable state, and the high barrier makes it very difficult for the system to jump into the equilibrium state. It is also interesting to note that both the stripe and trimer structures are anisotropic, while the interaction between the particles is purely isotropic. Indeed, this reflects a kind of symmetry breaking. In such a dense system, if particles are equally spaced from each other, the system would obtain a high energetic cost since the corona of each particle overlaps with all its
nearest neighbors. If the system chooses a stripe or trimer configuration, however, despite close packing with two nearest particles, a particle would keep away from other ones as much as possible and finally minimize the energetic cost.

As indicated in Fig. 1(d), the equilibrium state of the system would change from stripe to trimer with an increment of \( k_a \). For \( k_a = 200 \) as shown in Fig. 1(c), the observed metastable state has more stripe particles than the trimer particles, \( \phi_s < \phi_T \). In Fig. 1(e), we show how the stable values of the fractions \( \phi_i \) change with \( k_a \).

With increasing \( k_a \), \( \phi_T (\phi_s) \) increases (decreases) monotonically as expected, while the fraction of the disordered phase does not change much. The observed patterns all look similar to those shown in Fig. 1(b), except that the fractions of different phases are different. Therefore, starting from a random initial condition, the system would finally get trapped into a metastable mixed-phase state no matter what the value of \( k_a \) is. Indeed, this makes it hard to obtain very ordered structures in practical self-assembly processes and it is demanding to find a way to overcome this difficulty.

### B. Active case

We now put the system (still \( k_a = 200 \)) far from equilibrium by adding a nonzero active force to each particle, starting from a similar random initial condition as for the passive case. In Figs. 2(a)–2(d), we give typical snapshots of the system during the relaxation process for an intermediate level of active force \( F_a = 30 \). Very interestingly, the final state shows a perfect stripe phase [Fig. 2(d)], which is in sharp contrast to the metastable mixed-phase shown in Fig. 1(b) for \( F_a = 0 \). This stripe phase looks the same as the equilibrium one for \( k_a = 200 \) shown in Fig. 1(d). Therefore, the system successfully self-assembles into the demanded highly ordered state by making the particles active.

The transition from the initial disordered state to the final ordered state consists of three main steps. In the first step from Figs. 2(a) to 2(b), one can see that most of the disorder phase transforms into the more ordered stripe or trimer phase, and the remaining trimer-phase particles aggregate together to form a small island surrounded by the stripe phase. This trimer island will survive for some time, and since the stripe is more stable than the trimer according to the equilibrium phase diagram for \( k_a = 200 \), in the second step from Figs. 2(b) and 2(c), the trimer island will finally be eliminated and the system changes into a state dominated overwhelmingly by the stripe phase. Such a stripe-dominated phase still contains some disorder defects, and in the third step from Figs. 2(c) to 2(d), the system finally transforms into a nearly perfect stripe phase with no apparent defects by local rearrangement and relaxation (see the supplementary material, Movie 1). Accordingly, the time dependence of \( \phi_s \) is shown in Fig. 2(e). As can be seen, \( \phi_s \) increases rapidly at the very beginning to a relatively high value about 0.78 (see the orange cross), corresponding to the first step. Then, \( \phi_s \) keeps at a plateau \( \phi_s \approx 0.88 \) for some time. Clearly, the plateau is related to the metastable trimer island that will survive for some time before losing stability. The final slow increase in \( \phi_s \) to 1.0 corresponds to the third relaxation step. Note that the life time of the trimer island randomly changes from simulation run to run, but the trimer island can always be observed during the process.

The above observations clearly demonstrate that particle activity can induce very exciting behavior that is not available for the passive counterpart system. Surely, the results should be dependent on the activity level \( F_a \). In Figs. 3(a)–3(c), the final stationary states of the system for \( F_a = 10, 40, \) and 80 are presented. In contrast to the case of \( F_a = 30 \) shown in Fig. 2(d), these patterns are not fully ordered. For a relatively small activity \( F_a = 10 \), the trimer island cannot be eliminated by the surrounding stripe phase such that the final state is a mixture of stripe phase, trimer island, and some disorder defects. For \( F_a = 30 \), as we already described in Fig. 2(d), a highly ordered stripe structure emerges. If increasing the activity to \( F_a = 40 \), however, the final state would not be that ordered, as depicted in Fig. 3(b), wherein the system maintains some long range order defects.

![FIG. 2. Formation of a highly ordered stripe structure. (a)–(d) Representative configurations at the stage \( t = 10 \), \( t = 90 \), \( t = 140 \), and \( t = 290 \), respectively. The red dashed line in (b) depicts a trimer domain and two red arrows point to the direction that the trimer domain disappears. (e) Fraction of stripe phase \( \phi_s \) over time. Inset is a zoomed-in view of the area in red circle, and the four moments depicted by orange crosses correspond to (a)–(d) orderly. Note here \( F_s = 30 \).](image-url)
order but with many dynamic defect boundaries between ordered stripe clusters. With further increasing activity to a larger value, i.e., \( F_a = 80 \), the system turns into a totally disordered state as shown in Fig. 3(c). Therefore, there exists an optimal level of activity (here \( F_a = 30 \)) that favorably supports the formation of ordered stripe phase. Accordingly, the stable values of \( \phi_i \) (i = S, T, D) are depicted in Fig. 3(d), wherein \( \phi_S \) nonmonotonically changes with \( F_a \) and reaches the maximum about 1.0 for \( F_a \) within a small range around 30.

To get more information about the final stationary states of the system, we have further investigated the dynamic and static characteristics in terms of the diffusion coefficient \( D \) and the radial distribution function \( g(r) \), respectively. The diffusion coefficient \( D \) is calculated via \( D = \lim_{t \to \infty} \frac{1}{2t} \langle \Delta r^2(t) \rangle \), where \( \langle \Delta r^2(t) \rangle = \langle (r(t) - r(0))^2 \rangle \) is the mean square displacement (MSD) of a randomly chosen tagged particle with \( r(t) \) being the particle position at time \( t \). The radial distribution function \( g(r) \), defined as \( g(r) = \frac{1}{p} \langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(r - r_i) \delta(r - r_j) \rangle \) where \( p = N/V \) is the number density, characterizes the probability of finding a pair of particles at a distance \( r \) and thus reflects the structure of the system. In Fig. 3(e), \( D \) as a function of \( F_a \) is shown. With increasing \( F_a \), \( D \) starts from nearly zero at the initial stage and increases sharply at \( F_a = 40 \). This result indicates that the stable state of the system behaves like solids for small activity \( F_a \leq 40 \). We note here that the stable structure for \( F_a = 30 \), which is very ordered, is also very stable against thermal fluctuations since the diffusion coefficient \( D \) is zero. If activity is large, however, the system behaves more like fluids with large \( D \) and loses long range order, as, for example, depicted in Fig. 3(c) for \( F_a = 80 \). The effect of particle activity can also be reflected in \( g(r) \) as drawn in Fig. 3(f). Generally, \( g(r) \) shows main peaks at \( r/\sigma \approx 1, 2.7, \) and 5.3, corresponding to the typical nearest neighboring structures of the system. In particular, the peak at \( r/\sigma \approx 2.7 \) corresponds to the distance between neighboring parallel stripe segments and that at \( r/\sigma \approx 5.3 \) corresponds to the distance between next-nearest parallel stripes. One can see that the peaks at \( 2.7 \sigma \) exist for all the activities shown, suggesting that local stripe segments maintain with the variation of \( F_a \), and the distance between neighboring parallel segments remains nearly unchanged as can be observed for all the patterns shown in Figs. 3(a)–3(c) and 2(d). For not much strong activities \( F_a = 10, 30, \) and 40, the peaks at 5.3\( \sigma \) are remarkable, indicating the existence of some long-range order of parallel stripe patterns. The peak for \( F_a = 30 \) is highest among all them, corresponding to the most ordered stripe lattice given in Fig. 2(d). However, for a too strong activity, say, \( F_a = 80 \), the peak at 5.3\( \sigma \) disappears, indicating that the long-range stripe order is destroyed. All these findings clearly suggest that activity can impose twofold effects on this core-corona system: a proper level of activity can facilitate the emergence of ordered structures, while a large one may ruin the order and make

**FIG. 3** The impact of activity on the static and dynamic characteristics of the core corona system. [(a)–(c)] Representative long time stable configurations at \( F_a = 10, F_a = 40, \) and \( F_a = 80, \) respectively. (d) Stable values of the fractions \( \phi_i \) (i = S, T, D corresponding to stripe, trimer, and disorder, respectively) as a function of \( F_a \). (e) Diffusion coefficient \( D \) as a function of \( F_a \). (f) Radial distribution function \( g(r) \) at different activities.
The system order shows a nonmonotonic dependency on particle activity, consistent with Fig. 3(d).

A common way to understand the activity enhanced dynamic process is mapping such an active system to a passive system with an effective high temperature; thus, a test to this effective temperature ansatz is salutary. We do this test in a passive system by solely varying the temperature (represented as $k_B T$) at $k_s = 200$. In Fig. 4, $\phi_i$ ($i = S, T, D$) as functions of $k_B T$ are shown. Interestingly, as can be seen, $\phi_S$ shows a nonmonotonic dependency with $k_B T$ that first increases to a maximum and then drops down. That is, the temperature can impose twofold effects on the order, which a moderate temperature can accelerate the relaxation and increase the system order, while a high temperature would destroy the order. These results are greatly similar to an active case where a nonmonotonic effect on system order can also be observed [Fig. 3(d)]. However, note that the system order by solely changing the temperature can only reach a limit at 0.91 (Fig. 4), in contrast to a limit over 0.99 (nearly defect-free) in an activity-methodology. That means, activity indeed plays a role as effective temperature, but furthermore it acts better than temperature on the formation of highly ordered structures probably due to a memory effect within the persistent time (the thermal fluctuation here is Markovian).

The emergence of highly ordered stripe structures at an optimal level of activity ($F_a = 30$) demonstrated above, if achieved in practice, could be very promising for material design for important systems such as photonic crystal or template for lithography. Here, we try to give a qualitative understanding on this phenomenon with colored noise.

The difference of this activity from pure thermal fluctuation is that activity exerts persistence propulsion on the particle motion within the correlation time. If activity is too strong, e.g., $F_a = 100$ as shown by the black arrow, a metastable state would survive for a very long time against thermal fluctuation and the ordered state cannot be reached. If particle activity is presented, however, it acts as a kind of external driving force. The difference of this activity from pure thermal fluctuation is that activity exerts persistence propulsion on the particle motion within the correlation time. If activity is small, the propulsion or driving force is still weak and the system still stays in the metastable state. At a proper level of activity, the system may jump out of the local minimum of free energy into the ordered state with the lowest free energy, which is what we observed for $F_a = 30$. Since the barrier from the lowest minimum back to the metastable state is high, the system would stay stably in the ordered state. If activity is too small, e.g., $F_a = 80$, the system may jump out of the lowest minimum back to the metastable one, thus leading to the disordered state again. Thus, such a phenomenological description is quite qualitative and a theoretical analysis would be highly helpful; however, it is beyond the scope of the current study and may deserve a separate work.

FIG. 3(d) shows a nonmonotonic dependency with $k_B T$ corresponding to stripe, trimer, and disorder, respectively as a function of $k_B T$ at $k_s = 200$. The system is initialized in an almost perfect stripe-ordered structure ($F_a = 30$) and superpose a higher activity at some time, e.g., $F_a = 50$, to mimic the external damaging factor and remove it at a later time. When the damage is turned on, the ordered stripe state is destroyed as expected and $\phi_S$ drops to a lower value. Once the damage is removed, however, $\phi_S$ immediately jumps back to about 1.0 and the system recovers the ordered state again (see the supplementary material, Movie 2). Therefore, the ordered stripe state is quite stable and robust as long as the particle activity is maintained at the proper level.

The above results strongly suggest that a moderate level of activity can induce the self-assembly of highly ordered structures. Here, we try to give a qualitative understanding on this phenomenon in terms of a phenomenological free energy argument. As discussed in Subsection III A, the equilibrium state with the lowest free energy for $k_s = 200$ is actually the ordered stripe phase, while that observed mixed state [shown in Fig. 1(b)], with the simulation starting from a random initial condition, is a metastable state. Without activity, such a metastable state would survive for a very long time against thermal fluctuation and the ordered state cannot be reached. If particle activity is presented, however, it acts as a kind of external driving with colored noise. The difference of this activity from pure thermal fluctuation is that activity exerts persistence propulsion on the particle motion within the correlation time. If activity is small, the propulsion or driving force is still weak and the system still stays in the metastable state. At a proper level of activity, the system may jump out of the local minimum of free energy into the ordered state with the lowest free energy, which is what we observed for $F_a = 30$. Since the barrier from the lowest minimum back to the metastable minimum is high, the system would stay stably in the ordered state. If activity is too strong, e.g., $F_a = 80$, the system may jump out of the lowest minimum back to the metastable one, thus leading to the disordered state again. Surely such a phenomenological description is quite qualitative and a theoretical analysis would be highly helpful; however, it is beyond the scope of the current study and may deserve a separate work.
So far, we have studied the results for $k_s = 200$, where the equilibrium state is the stripe phase. It is then interesting to investigate the phase behaviors for other values of $k_s$. In Figs. 6(a)–6(d), four representative stable patterns for $k_s = 300$ with $F_a = 20, 60, 80$, and 120 are shown, respectively. For a low activity $F_a = 20$ in (a), the system is now typically a mixture of trimer phase and stripe phase. For a moderate activity $F_a = 60$ in Fig. 6(b), interestingly, a highly ordered trimer phase appears. The formation of such an ordered trimer phase is similar to that of the stripe phase shown in Fig. 2, involving a relatively fast process forming several big clusters of trimer phases and a slow relaxation process healing the grain boundaries (see the supplementary material, Movie 3). However, there are still many defects doped linearly inside the lattice, which is slightly different from a $k_s = 200$ case that the system contains nearly no defects. This is due to the fact that these defects are usually trapped as dimers, and they could hardly be merged into trimers only when at least 3 of them meet. Note that this ordered structure also has a self-healing feature. Further increasing $F_a$ to 80 in Fig. 6(c), such a trimer superlattice becomes unstable and the system contains a few clusters of the trimer surrounded by a disordered phase or small stripe phase. Compared to the state shown in Fig. 6(a), the system now is more “living,” i.e., the clusters may split into small pieces and then merge again, while that in Fig. 6(a) is static. If the activity is even higher, say, for $F_a = 120$ in Fig. 6(d), the system behaves like liquids and becomes disorder. The nonmonotonic dependency between activity $F_a$ and the fraction of trimer phase $\phi_T$ is very similar to the $k_s = 200$ case.

It is interesting to note that the activity-induced ordered structure for $k_s = 300$ and $F_a = 60$ is the trimer phase rather than the stripe phase, while the equilibrium state for $k_s = 300$ is still the stripe phase as suggested in Fig. 1(d). This indicates that activity can not only facilitate the self-assembly process to reach the ordered structure but also can induce a new structure that is not available in the equilibrium counterpart system. It is then very demanded to obtain a global picture by investigating the whole (nonequilibrium) phase behavior in the parameter plane spanned by $F_a$ and $k_s$. In Figs. 7(a)–7(c), the contour plots of $\phi_S$, $\phi_T$, and $\phi_D$ in the $(F_a, k_s)$ plane are presented, respectively. In Fig. 7(a), one can see that $\phi_S$ is highest in the region of small $k_s$ and $F_a$ and disappears if $k_s$ exceeds some threshold value. In Fig. 7(b), the distribution of $\phi_T$ is just complementary to that of $\phi_S$; i.e., it is highest in the region where $k_s$ and $F_a$ are large. The transition from stripe to trimer approximately takes place at $k_s \approx 250$, which is not sensitive to the value of $F_a$ in the moderate range. Note that the transition from stripe to trimer for an equilibrium system takes place at nearly $k_s \approx 650$, suggesting that activity strongly shifts the transition point. Therefore, in a broad range of $k_s \in (250, 650)$, activity can induce a transformation from stripe to trimer. For a given $k_s$, both $\phi_S$ and $\phi_T$ show nonmonotonic dependencies on $F_a$, as can be seen from Figs. 7(a) and 7(b). In Fig. 7(c), it is shown that the system is quite disordered in the left-up and right-bottom corners of the parameter plane. In the diagonal region, $\phi_D$ is zero, indicating that the system is in purely ordered state without defects. The optimal value of $F_a$ seems to increase linearly with $k_s$, as suggested by the contour plot.

FIG. 6. Representative long time stable configurations at $k_s = 300$ for $F_a = 20, 60, 80$ and 120, corresponding to (a)–(d), respectively.

FIG. 7. Nonequilibrium phase diagram of long time stable value of (a) $\phi_S$ colored in green, (b) $\phi_T$ colored in orange, and (c) $\phi_D$ colored in blue, respectively. The color bar attached at the right-side of each phase diagram is at a range of (0, 1.0).
IV. DISCUSSION

In this work, $D_t$ and $D_a$, the translational and rotational diffusion coefficients, are coupled by $D_a = 3D_t / r^2$ in the low-Reynolds-number regime. However, in many cases of active Brownian particles (ABPs), $D_a$ can be independently controlled. Thus, it is helpful to study the effect of rotational rate by setting $D_t$ as an independent parameter. We found that the system order, e.g., stable value of $\phi_S$ at $k_b = 200$, shows a nonmonotonic dependency with $D_t$ (results are not shown here). The relation between $\phi_S$ and $D_t$ is similar to that between $\phi_S$ and $F_a$ as shown in Fig. 3(d) where the same nonmonotonic relation can be observed, suggesting a mapping between $D_t$ and $F_a$. Actually, in a more general definition, activity is represented as the Péclet number which is defined as $Pe = v_p / \sqrt{D_t/D_a}$, where $v_p = F_a / y$ is the propelled speed. That means activity is proportional to $F_a$ and meanwhile inversely proportional to $\sqrt{D_t}$. The underlying picture should be that activity is proportional to the persistence length $L = v_p \tau_r$ ($\tau_r \sim 1/D_t$) that the particle will move along the direction of its initial orientation in a persistence time before its direction is changed. That is, a very small $D_t$ could be equivalent to a strong activity (or high value of $F_a$) that could easily destroy the system order, while conversely a large $D_t$ corresponds to a weak activity (or low value of $F_a$) that could hardly affect such a highly crowded system.

Besides, we here only consider one specific density that could create stripe-like and trimerlike patterns. It would be interesting to discover more densities to check the activity enhanced assembly strategy. First, one should exclude a dilute system that each particle has enough space to freely move. In this case, active core corona particles can be considered as ABPs with an effective radius that equals to the cut of corona potential, and increasing activity would make the system phase separate into a dense phase and a gas phase which is just the so-called motility induced phase separation (MIPS) phenomenon. Beyond that, at some dense systems, for example, $c \approx 0.31$ and $c \approx 0.61$, we have, respectively, observed a highly ordered dimer structure and a highly ordered tetramer structure, if introducing a moderate activity and keeping other parameters the same as in Fig. 2. Therefore, we believe that such an activity enhanced assembly strategy can also work well at a wider density regime and deserves more future studies.

V. CONCLUSION

In summary, we have theoretically studied the self-assembly process of active core corona particles by using a two-dimensional overdamped Langevin dynamics simulation. This system with typically two-length scales owns the possibility to form various anisotropic and superlattice structures. However, such a system would generally be trapped into a metastable state with many defects and the transition from a metastable state to a thermodynamically favored one involves many local structural rearrangements, which makes the emergence of target ordered structures occur at an unreachable long time scale. However, if exerting a moderate active force to each particle, such a metastable state can successfully cross the energy barrier leading to a large-scaled and highly ordered stripe or trimer lattice. In addition, these active induced ordered structures are stable against thermal fluctuations even when the activity is removed and can spontaneously heal strong damages as long as the activity keeps at a proper level. Our results demonstrate clearly that activity can be used as a new design strategy for the self-assembly process.

It would be interesting to test our model in experimental systems, for instance, a dense system of Janus particles coated by microgels in an alternating electric field. The particles could exhibit spontaneous motility in such a field and repel each other due to the ambient soft microgels. In practice, spring potential may not exactly hold when two coronas are strongly extruded, while one can alternatively use an external field to achieve a more robust repulsive interaction. For example, Osterman et al. used an external magnetic field to achieve the repulsion between superparamagnetic spheres that are trapped in a thin wedge-shaped cell and softened the repulsion by changing the cell thickness. Since the two key ingredients, corona and activity, are ubiquitous in many real systems and widely studied both theoretically and experimentally, we hope that our results could open new perspectives to the fabrication of similar highly ordered and self-healing structures and provide new insights into defect engineering in the material field.

SUPPLEMENTARY MATERIAL

See the supplementary material for the formation process of the highly ordered stripe structure in movie 1, the highly ordered trimer lattice in movie 3, and the self-healing process in movie 2.

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REFERENCES