Emergence of Living Chiral Superlattice from \textit{Biased-Active} Particles

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We introduce for the first time a general model of \textit{biased-active} particles, where the direction of the active force has a biased angle from the principle orientation of the anisotropic interaction between particles. We find that a highly ordered living superlattice consisting of small clusters with dynamic chirality emerges in a mixture of such biased-active particles and passive particles. We show that the biased-propulsion-induced instability of active-active particle pairs and rotating of active-passive particle pairs are the very reason for the superlattice formation. In addition, a biased-angle-dependent optimal active force is most favorable for both the long-range order and global dynamical chirality of the system. Our results demonstrate the proposed \textit{biased-active} particle providing a great opportunity to explore a variety of new fascinating collective behaviors beyond conventional active particles.

Since active systems can be driven far from equilibrium\cite{1} by continuously consuming energy supplied internally or externally, understanding collective behaviors of such systems is of great importance for revealing the mystery of living systems and further for manufacturing smart materials\cite{2}. To date, many research interests have been paid on the effect of active motion on the dynamics, and a great array of collective behaviors that cannot be manifested in equilibrium systems have been reported, such as motility-induced phase separation\cite{3,4}, anomalous density fluctuations\cite{5,6}, and spontaneous flow\cite{7}.

Recently, it is recognized that designing complex interactions between active particles rather than simply changing the active force is very important for guiding the formation of collective behaviors\cite{2}. Chemically synthesized Janus particles is one of the examples, where self-propulsion may arise from non-uniform properties of the Janus particles\cite{8-11} while the interaction between these particles can be strongly anisotropic\cite{12}. By controlling the amplitude of anisotropic interactions, S.Granick and coworkers\cite{13–15} reported several interesting new dynamic phase states such as rotating pinwheels. It should be a significant step forward in active-particle designing if new methods beyond conventional ones are proposed.

In this Letter, we propose a conceptually new design of active particles focusing on the correlation between active motion and anisotropic interaction, namely, \textit{biased-active} particles where the direction \textbf{n} of active force has a biased angle $\theta$ from the principle orientation $\textbf{q}$ of the anisotropic interaction (Fig.1). The variation of $\theta$ offers a rich design space for dynamic self-assembly, providing a great opportunity to explore a variety of new fascinating collective behaviors beyond conventional active particles. As an example, we report the emergence of a striking superlattice structure with dynamic chiral clusters (DCCs) in a mixture of such biased-active particles and passive particles for $\theta$ larger than some threshold values. We find that such biased propulsion may on one hand lead to instability of active particle (AP) clusters formed due to anisotropic interaction, and on the other hand induce the rotation motion of an AP around the passive particle (PP) it attached. As a consequence, many ordered hexagonal DCCs, each with six APs rotating around a PP, are formed. These DCCs may finally organize into a superlattice with long range order and hexagonal symmetry which would not be observed neither in the counterpart equilibrium system nor in the conventional active particle system.

The system contains $N_a$ APs and $N_p$ PPs of the same diameter $\sigma$. Each AP is of Janus type containing two half spheres which allows us to define an orientation unit vector $\textbf{q}$, pointing to the face (red side) as shown in Fig.1. Besides, AP is also subjected to a self-propulsion force with amplitude $F_a$ along a direction given by a unit vector $\textbf{n}$ with a biased angle $\theta$ from $\textbf{q}$. For a pair of APs $i$ and $j$, the interaction $U_{ij}$ contains two terms,

\begin{equation}
U_{ij}(\textbf{r}_{ij}, \textbf{q}_i, \textbf{q}_j) = U_{WCA}(\textbf{r}_{ij}) + U_{AN}(\textbf{r}_{ij}, \textbf{q}_i, \textbf{q}_j),
\end{equation}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig1.png}
\caption{Schematic of the biased-active particle with a biased-angle $\theta$ between active direction \textbf{n} and the anisotropic interaction orientation $\textbf{q}$. The red side is attractive and the green is repulsive.}
\end{figure}
where \( \mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i \) is the vector pointing from particles \( i \) to \( j \), \( r_{ij} = |\mathbf{r}_{ij}| \) is the corresponding distance. The first term \( U_{WCA}(r_{ij}) \) denotes an isotropic excluded volume interaction given by the WCA potential \([16]\),

\[
U_{WCA}(r_{ij}) = 4 \epsilon \left[ \left( \frac{\sigma}{r_{ij}} \right)^{12} - \left( \frac{\sigma}{r_{ij}} \right)^{6} + \frac{1}{2} \right] \text{ if } r_{ij} < 2^{1/6} \sigma, \text{ and zero otherwise, with } \epsilon \text{ the interaction strength. The second term } U_{AN}(\mathbf{r}_{ij}, \mathbf{q}_i, \mathbf{q}_j) \text{ is the anisotropic Yukawa interaction potential given by } [17, 18]
\]

\[
U_{AN}(\mathbf{r}_{ij}, \mathbf{q}_i, \mathbf{q}_j) = \frac{C \exp[\frac{-\lambda(\mathbf{r}_{ij} - \mathbf{\sigma})}{\mathbf{r}_{ij}^2}]}{\mathbf{a}} (\mathbf{q}_i - \mathbf{q}_j) \cdot \mathbf{r}_{ij}, \tag{2}
\]

where \( C \) denotes the interaction strength and \( \lambda^{-1} \) gives the corresponding screen length. According to this anisotropic interaction, two APs \( i \) and \( j \) attract each other most strongly if their orientation vectors \( \mathbf{q}_i \) and \( \mathbf{q}_j \) pointing to each other, i.e., in a face-to-face configuration, while they repel each other most strongly in back-to-back position. The interactions \( U_{ij} \) between any two PP are isotropic and just given by the WCA potential with same parameters as those for APs. For the interactions between a pair of PP and AP, we assume that PP only attracts the face side of AP and has no interactions with the back side. The interaction potential is also given by Eq.\,(2), but with a stronger strength \( C' \) for active-passive pairs than \( C \) for active-active pairs.

The evolution equation governing the dynamics of \( \mathbf{r}_i \) \((i = 1, 2, \ldots, N)\) with \( N = N_a + N_p \) is then given by

\[
\dot{\mathbf{r}}_i = \frac{D_t}{k_B T} \left( \sum_{j \neq i}^N \frac{\partial U_{ij}}{\partial \mathbf{r}_i} + F_n \mathbf{n}_i \right) + \mathbf{\xi}_i, \tag{3}
\]

where \( k_B \) denotes the Boltzmann constant, \( T \) is the temperature, and \( \mathbf{\xi}_i \) is the thermal fluctuation satisfying the fluctuation-dissipation relationship \( \langle \mathbf{\xi}_i(t) \mathbf{\xi}_i(t') \rangle = 2D_t \mathbf{1} \delta(t - t') \) with \( D_t \) the translational diffusion coefficient and \( \mathbf{1} \) the unit tensor. \( F_n \) is the amplitude of active force and is set to be zero for PPs.

For an AP, the direction of active force \( \mathbf{n}_i \) (and thus \( \mathbf{q}_i \)) changes via random rotational diffusion. In addition, the anisotropic interaction also exerts a torque on the particle and thus leads to the change of particle orientation. Therefore, the dynamic equation of \( \mathbf{q}_i \) can be written as,

\[
\dot{\mathbf{q}}_i = -\frac{D_r}{k_B T} \left( \sum_{j \neq i}^N \frac{\partial U_{AN}(\mathbf{r}_{ij}, \mathbf{q}_i, \mathbf{q}_j)}{\partial \mathbf{q}_i} \right) + \mathbf{\eta}_i \times \mathbf{q}_i, \tag{4}
\]

where the first term describes the torque exerted by the aforementioned anisotropic interaction to particle \( i \), and \( \mathbf{\eta}_i \) is the rotational fluctuation of the active direction satisfying \( \langle \mathbf{\eta}_i(t) \mathbf{\eta}_i(t') \rangle = 2D_r \mathbf{1} \delta(t - t') \) with the rotational diffusion coefficient \( D_r = 3D_t/\sigma^2 \).

Simulations are performed in a \( L \times L \) two dimensional square box with periodic boundary conditions. \( \sigma, k_B T, \) and \( \tau = \sigma^2/(10D_t) \) are chosen as the dimensionless units for length, energy and time, respectively. We fix \( N = 2100 \) with \( N_a/N_p = 6, \varepsilon = 1.0, C = 3.0, \lambda = 3\sigma^{-1} \)

\[
\text{during the simulations if not otherwise stated. The box length is } L = 60 \text{ corresponding to a packing fraction } \phi = 0.46, \text{ and the simulation time step is } \Delta t = 10^{-4} \tau.
\]

We assume a stronger interaction among passive-active pairs than active-active ones by setting \( C' = 2C \) in the current work. The active force \( F_a \) and biased angle \( \theta \) are chosen as variable parameters. All simulations start from random initial conditions and run for enough long time to ensure the system has reached a stationary state.

Firstly, we consider a typical angle \( \theta = \pi/2 \), where the active force direction \( \mathbf{n}_i \) for particle \( i \) \((i = 1, \ldots, N)\) is perpendicular to the principle direction of anisotropic interaction \( \mathbf{q}_i \). Very interestingly, it is observed that a highly ordered superlattice consisting of many living chiral clusters emerges spontaneously if the active force is within a certain appropriate range. In Fig\,2(a)-(d), the typical snapshots of the system are depicted for different active forces \( F_a = 0, 6, 16, \text{ and } 26, \) respectively. Without activity \((F_a = 0)\), the particles tend to form
small clusters with the face sides attracted together due to the anisotropic interaction, or clusters with several APs attached to a PP due to attractions between AP–PP pairs (Fig 2(a)). One can also find few hexagonal clusters wherein one PP is surrounded by six APs, which are quite ordered in short range, nevertheless, the whole system is disordered in long range. Note that this disordered state is quite stable with respect to thermal noises $\xi$ in the system. For a small active force, say $F_a = 6$ as shown in Fig 2(b), much more clusters with one PP surrounded by six APs (the inset in Fig 2(b)) emerge. Interestingly, the APs rotate clockwise around the central PP continuously, demonstrating a novel type of dynamic chirality. Some long-range order already appears in this state, nevertheless, there are still many non-hexagon clusters remaining in the system. For an appropriate level of activity as shown in Fig 2(c) for $F_a = 16$, remarkably, a perfectly ordered superlattice emerges with hexagon structures in both long and short ranges. In this superlattice state, each PP is accompanied by six APs to form a hexagon cluster, and all the $N_p$ clusters rotate in the same clockwise direction. If the active force is too large, however, such ordered structure is destroyed again as shown in Fig 2(d) for $F_a = 26$, wherein the long-range order is lost and many hexagon clusters are broken. Supplemental movies are available for these $F_a$.

Clearly, the living one-plus-six dynamic chiral clusters (DCCs) play important roles in the system’s collective behaviors. With the increase of active force $F_a$, we find that the fraction of DCCs (left axis in Fig 2(e)) undergoes a maximum value, where $R_{cc} = N_{cc}/N_p$ with $N_{cc}$ the number of DCCs. For small or large $F_a$, $R_{cc}$ is small (but not zero), while it reaches nearly 1.0 within an intermediate range of $F_a$. To characterize the long-range order of the system, we measure the global order by the parameter $\Psi = N_p^{-1} \sum_{j=1}^{N_p} g_0^j$ for the lattice formed by PPs, where the overbar denotes averaging over time. $g_0^j = 1/6 \sum_{k \in N(j)} \exp (i \theta_{kj})$ denotes the local order parameter for the $j$th PP with $k \in N(j)$ running over its 6 nearest PP neighbors and $\theta_{kj}$ the angle between an arbitrary axis and $\mathbf{r}_{kj}$. Fig 2(e) also shows the dependence of $\Psi$ (right axis) on $F_a$, wherein a clear-cut maximum can again be observed, i.e., $\Psi$ increases from a relatively small value at $F_a = 0$, to a value close to 0.9 for intermediate values of $F_a$ corresponding to a very ordered superlattice state, and then decreases sharply to a small value again for $F_a \geq 30$. Clearly, the fraction of DCCs $R_{cc}$ is highly correlated with the global order parameter $\Psi$. Such findings clearly demonstrate that an optimal level of particle activity drives the formation of the highly ordered superlattice.

Another nontrivial feature of the superlattice as shown in Fig 2(c) is the rotation of DCCs, i.e., the peripheral six APs rotate clockwise around the central PP. Interestingly, the average rotation speed $\bar{\omega}$ (calculated for APs stably rotated around the PP they attach) also depends non-monotonically on the active force as shown in Fig 2(f) (left axis). For $F_a = 0$, although some hexagon clusters also exist, they just randomly swing and $\bar{\omega}$ is nearly zero. With increase of $F_a$, the rotation speed $\bar{\omega}$ also increases till it reaches a maximum value $\bar{\omega} \approx 24$, after which $\bar{\omega}$ decreases again. Note that in the range of $F_a$ where ordered superlattice states can be observed ($\Psi \approx 1$), the rotation speeds $\bar{\omega}$ are also nearly the largest. Such nearly synchronized rotation of the DCCs introduces global dynamic chirality of the whole system, which may be measured conveniently by an order parameter $\chi = N_p^{-1} \sum_{i=1}^{N_p} \bar{\omega}_i$, where $\bar{\omega}_i$ is the average rotation speed $\bar{\omega}$ if AP-i rotates anti-clockwise (clockwise) and the overbar again denotes averaging over time. Fig 2(f) shows the variation of $\chi$ with $F_a$ (right axis), where a non-monotonic behavior is present too. With the increase of active force, $\chi$ decreases from nearly zero at $F_a = 0$ and then approaches a platform of $\chi \approx 1$ representing that all active particles are rotating in the same clockwise direction, and finally increases again to $\chi \approx 0$ at larger values of $F_a$. In addition, the region of $F_a$ wherein the dynamic chirality $|\chi|$ is maximal also coincides with that for the optimal long-range order $\Psi$.

FIG. 3: Schematic of the formation and breaking mechanism of DCC. The red arrows are the rotation directions of AP–PP pairs. Taking the $\theta = 0.5\pi$ as an example, (a) both of the AP–AP pairs and the AP–PP pairs are formed for $F_a = 0$. (b) Increase $F_a$ breaks the AP–AP pair into single APs, and the particle pairs start to rotate. (c) Single APs are attracted by PPs due to the stronger anisotropic interaction between AP–PP pairs. (d) For large enough $F_a$, the DCC also falls apart.
AP-pairs would not take effect if attraction between the two APs and the pair will break. Given that the active force is not too large, the AP will rotate around the PP clockwise (note that such superlattice state can even be observed for \( \theta = \pi \), while all the DCCs no longer rotate. In Fig.4(b), the contour plot of \( \chi \) is also shown in the plane of \((F_a, \theta)\), wherein one can easily see that an optimal level of active force with appropriate range of biased angle \( \theta \) are most favorable for the global dynamics chirality of the system. Note that for \( \theta = -\theta_0 \), \( \Psi \) is the same as for \( \theta = 0 \), while \( \chi \) has the opposite value (\( \chi < 0 \) for \( \theta > 0 \) and \( \chi > 0 \) for \( \theta < 0 \)).

In conclusion, we have systematically investigated the dynamic self-assembly of a mixture of biased-active and passive particles. The peculiar biased character of the active component, namely, the active force is exerted along a different direction from the orientation of anisotropic interaction, leads to the emergence of a remarkable living superlattice with global dynamic chirality and highly ordered hexagonal structure in both short and long ranges. Such a superlattice state cannot be observed in the absence of active force or biased angle, demonstrating the nontrivial roles of the both factors. To synthesize the biased-active particle experimentally, we suggest a protocol that an isotropic particle can be coated by two different layers of materials separately with the aimed biased angle, one of which produces anisotropic interaction and the other provides self-propulsion. Therefore, we believe that the biased-active particle model provides a conceptually new approach to design smart self-assembled structures, and our work may inspire a variety of following theoretical and experimental investigations in future.

Acknowledgments

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