Rod-assisted heterogeneous nucleation in active suspensions

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Motility induced phase separation as well as the nucleation process in active particle systems has gained extensive research attention very recently. Most studies so far have considered homogeneous cases without the influence of foreign seeds or impurities; however, the heterogeneous nucleation process and phase behaviors of a suspension of active Brownian particles by introducing a rod-like passive seed. We found that such a seed can exponentially accelerate the nucleation rate and thus readily induce phase separation of a dilute active system, while a homogeneous one with the same volume fraction still maintains a single phase. It is observed that the seed would automatically detach from the dense phase after the completion of phase separation instead of staying inside as an impurity. Interestingly, we found that the phase behavior is re-entrant with the activity: single-phase states exist at both high and low activities, with phase separated states in between. Our results demonstrate that heterogeneous nucleation in an active system can show novel behaviors with respect to its passive counterpart, and pave the way for more future studies in relevant fields.

I. Introduction

Active systems consisting of self-propelled objects have been one of the most exciting topics in recent years and attracted great research interest in soft condensed matter and non-equilibrium physics. Examples of active systems can range from very large scales in meters like schools of fish or flocks of birds, to very small scales in microns of natural microswimmers like algae and bacteria, and of artificial microswimmers like Janus spheres and chiral particles. These systems are usually far from equilibrium and can show a range of fascinating collective behaviors including phase separation, active turbulence, enhanced self-assembly, and so on. It is reported that self-propelled particles without any intrinsic alignment rules, known as active Brownian particles (ABPs), can spontaneously phase separate into solid-like and gas phases, wherein however the volume fraction is far below close packing. This phenomenon in active systems has come to be known as motility induced phase separation (MIPS) and has been observed in both simulation and experimental systems.

Many studies have been done to understand the underlying mechanism of MIPS. For instance, Redner et al. proposed a simplified kinetic model to explain MIPS and obtained analytically a phase transition boundary. They argued that the condition for phase separation is that a particle would be trapped in a cluster before it can escape when the collision time becomes shorter than the rotational diffusion time. Their results suggested that both high density and high activity of active particles can facilitate phase separation. In subsequent work, combined with classical nucleation theory (CNT), analogous to an equilibrium system, they further obtained the effective free energy analytically and the binodal curve. Other important studies include the effective Cahn–Hilliard theory, the effective pressure argument and a scalar field theory. Note that when the density decreases asymptotically to a critical value at the binodal, phase separation as well as nucleation becomes very difficult due to an increasing free energy barrier, and it would occur at a prohibitively long time scale such that it is hard for a conventional simulation run to detect such a rare event. Recently, D. Richard et al. studied the nucleation kinetics and the microscopic pathway of ABPs near the binodal, and they found a qualitative behavior for the nucleation rate as a function of density as for a passive suspension undergoing liquid–vapor separation.

For a supersaturated passive colloidal system, the crystallization process also suffers from crossing the free energy barrier of initial nucleation. However, in practice one can add some artificial seeds or a substrate into such a homogeneous system to help the nucleation, which is known as heterogeneous nucleation. For instance, A. Cacciuto et al. theoretically studied the heterogeneous nucleation process by adding a spherical seed into a supercooled colloidal system. They found that the free energy barrier of nucleation is apparently reduced as the seed size increases and thus the nucleation rate is greatly
enhanced. Besides, as the small nucleus grows to a precritical size, it can detach from the seed’s surface and thus such a seed again becomes free to produce new crystals. Subsequent experimental work by E. Allahyarov et al. confirmed such phenomena where the seed favors crystallization only during the initial growth.\(^4\) Furthermore the heterogeneous nucleation on a substrate was also studied in terms of both the nucleation pathway\(^4\) and nucleation rate.\(^4\) However, to the best of our knowledge, heterogeneous nucleation as well as the phase behavior in active particle systems has not been specifically studied yet.

Motivated by this, here in the present work we have studied the heterogeneous nucleation in a suspension of ABPs by introducing a rod-like seed, using two-dimensional overdamped Langevin dynamics simulation. The system is chosen to be so dilute that a homogeneous nucleation event could not happen in a reachable time scale. Upon adding the seed into this active suspension, we found that the nucleation process can be considerably accelerated, and the system can readily phase separate into a dilute- and a dense-phase. The mean nucleation time is shown to decrease exponentially with the length of the rod. Besides, we found that such a rod would detach from the generated cluster after the completion of phase separation, which is reminiscent of the sphere-assisted heterogeneous nucleation in passive colloidal systems\(^4\), mentioned above, and the time cost for detachment varies non-monotonically with the rod length. Furthermore, we have studied the phase behaviors by varying the activity with fixed rod length. Interestingly, we found that the phase behavior is re-entrant with the activity in that both low and high activity result in a single phase, while a moderate one can induce phase separation. Such a counter-intuitive phase behavior seems contrary to the general understanding that a higher activity can always promote phase separation better. Subsequent analysis indicates that the nucleation becomes harder as the activity increases such that the observed single-phase state at very high activity is actually a meta-stable one with a high nucleation barrier, and it is hard for the nucleation process to take place in a reachable time scale. Our results can offer better understanding of the heterogeneous dynamics of active systems and pave the way for more future studies in this field.

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

**II. Simulation method**

We study a two dimensional system composed of a rod immersed in a bath of active Brownian particles (ABPs) with diameter \(\sigma\), as shown in Fig. 1. The rod is discretized into \(L\) beads, each of size (diameter) \(\sigma\). All pair interactions between particles (ABPs or beads) are modeled by the purely repulsive Weeks–Chandler–Andersen (WCA) potential:\(^4\)

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

where \(r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|\) denotes the distance between two particles \(i\) and \(j\) (with position vectors given by \(\mathbf{r}_i\) and \(\mathbf{r}_j\), respectively), and \(\varepsilon\) represents the strength of the WCA potential. The dynamics of ABPs are described by the following overdamped Langevin equations:\(^1\)

\[
\dot{\mathbf{r}}_i = -\frac{1}{\gamma}\nabla U_{\text{WCA}}(r_{ij}) + \mathbf{F}_i + \mathbf{n}_i + \xi_i(t)
\]

\[
\dot{\theta}_i = \eta_i(t)
\]

where \(\mathbf{F}_i = -\sum_{j \neq i} \nabla_{\mathbf{r}_j} U_{\text{WCA}}(r_{ij})\), and \(\mathbf{n}_i\) represents the strength of the active force with orientation specified by the unit vector \(\mathbf{n}_i = (\cos \theta_i, \sin \theta_i)\). \(\xi_i(t)\) is a Gaussian white noise vector with \(\langle \xi_i(t) \rangle = 0\), \(\langle \xi_i(t)\xi_j(t') \rangle = 2D_r \delta(t-t')\), where \(\mathbf{1}\) is a unit tensor, and \(D_r = k_B T/\gamma\) denotes the translational diffusion coefficient of a passive particle in the dilute-limit with \(k_B\) the Boltzmann constant, \(T\) the temperature and \(\gamma\) the friction coefficient. \(\eta(t)\) is also a stochastic vector and Gaussian distributed with zero mean and has time correlations given by \(\langle \eta(t)\eta(t') \rangle = 2D_\theta \delta(t-t')\), where \(D_\theta\) denotes the rotational diffusion coefficient given by \(D_\theta = 3D_r/\sigma^2\) in the low-Reynolds-number regime. The rod is modeled as a rigid body described by two parameters: the center-of-mass position vector \(\mathbf{r}_R\) and the orientation angle \(\theta_R\). The dynamics of this rod is decomposed into a parallel and a perpendicular component with respect to its axis and an angular component.

![Fig. 1](https://example.com/figure1.png)

**Fig. 1** The illustration of a rod immersed in an active bath. Active particles are represented by blue spherical particles, while the rod with connected beads is colored green. Such a rod is modeled as a rigid body and the dynamics of it is decomposed into a parallel and a perpendicular component with respect to its axis and an angular component.
where $\mathbf{M}$ denotes the total torque, and $\mathbf{F}_{\lambda, \perp}$ and $\mathbf{F}_{\lambda, ||}$ denote the parallel and perpendicular components of the total repulsive force from ABPs, respectively. $\gamma_{\lambda k}$ and $\xi_{R, k}$ ($k = \perp, ||, r$) denote the friction and thermal noises of these three degrees of freedom. Following the relation $\left\langle \xi_{R, k}(l) \right\rangle = 0$, $\left\langle \xi_{R, k}(l)\xi_{R, k}(l') \right\rangle = 2k_BT\gamma_{R, k}\delta(l - l')$. The values of $\gamma_{R, k}$ are, according to the long-thin rod approximation, given by:

$$\gamma_{R, ||} = \frac{2L^2}{3(\ln L + \delta_||)^2}, \quad \delta_|| = -0.207 + 0.980L^{-1} - 0.133L^{-2}$$

$$\gamma_{R, \perp} = \frac{4L^2}{3(\ln L + \delta_\perp)^2}, \quad \delta_\perp = 0.839 + 0.185L^{-1} + 0.233L^{-2}$$

$$\gamma_{R, r} = \frac{2L^3\sigma_\perp}{27(\ln L + \delta_r)}, \quad \delta_r = -0.662 + 0.917L^{-1} - 0.050L^{-2}$$

Simulations are performed in a square box with edge length $L = 150\sigma$ with periodic boundary conditions. We use $\sigma$ and $\epsilon$ as basic units of length and energy, and set $\gamma = 1$, and $k_BT = 0.1$, and then one can get $\sigma^2/\epsilon$ as the unit of time. If not otherwise stated, we consider a system containing 9000 ABPs, corresponding to an area density $\rho = N\sigma^2/(4L^2) \approx 0.314$, which is above the binodal of MIPS. The stochastic Euler algorithm is employed to simulate the dynamic equations with a time step $\Delta t = 2 \times 10^{-5}\tau$.

III. Results and discussion

1. Comparison between homogeneous and heterogeneous cases

We first consider a homogeneous case where the system consists of only ABPs with fixed particle activity $F_a = 20$. Fig. 2(a) shows a typical stationary configuration after a long enough simulation run, starting from a random initial condition. Obviously, the system remains in a single-phase state. A further validation can be seen in Fig. 2(c), which depicts the distribution of local density $P(\rho)$ obtained by an ensemble of configurations after long time simulation runs. As can be seen, the orange curve corresponding to a homogeneous case shows one single peak at the overall system density (here $\rho \approx 0.314$) approximately, indicating a single-phase state. Besides, we have also studied the nucleation process by analyzing the growth of the largest cluster. This can be done by counting the number of particles $N_c$ in the largest cluster rescaled by the total particle number $N$, as shown by the curve in Fig. 2(d). During the whole range of time considered, $N_c/N$ stays at a very low value near zero. That means that the nucleation of the homogeneous case here can be hardly completed in a reachable time scale and thus the system shows a single-phase state as we have observed in Fig. 2(a).

Note that in practice, in order to accelerate the nucleation rate, a broadly used method in passive systems is introducing seeds into such homogeneous systems, which is known as heterogeneous nucleation. Here we adopt this method and add a rod-like seed into this active system. In Fig. 2(b), a typical stationary configuration of this heterogeneous case with rod length $L = 20$ is shown. In contrast to the homogeneous case, the system can clearly phase-separate into a dense phase and a dilute phase. This can be further shown by $P(\rho)$ in Fig. 2(c), where the green curve corresponding to the heterogeneous systems has two distinct peaks located at $\rho \approx 0.15$ and $\rho \approx 0.9$, respectively. The heterogeneous nucleation process is shown by the green curve in Fig. 2(d). Clearly, after a short induction time (i.e., nucleation time $\tau$), $N_c/N$ can increase sharply to a stationary value of about 0.8, suggesting the completion of phase separation.

2. Effects of the seed size on nucleation

The above results suggest that introducing a rod-like seed into the active suspension can greatly enhance the nucleation process and finally induce phase separation. To proceed, in this part, we study the effects of the seed size on the nucleation process. In Fig. 3(a)–(c), $N_c/N$ as a function of time for 30 independent runs is shown, corresponding to three different rod sizes $L = 4, 6$ and 10, respectively. For a short rod, e.g., $L = 4$ shown in Fig. 3(a), only a few curves of $N_c/N$ are observed to increase to a stationary value at about 0.6 after long nucleation times; however, most of the remaining curves stay at the bottom during the whole time range, indicating the difficulty for the nucleation process. Increasing $L$ to 6 (Fig. 3(b)), more curves of $N_c/N$ can raise up to a stationary value while still many curves cannot, which means that the nucleation now becomes easier but still difficult. Further increasing $L$ to 10 (Fig. 3(c)), all curves of $N_c/N$ can reach a stationary value after a short nucleation time. That is, all systems in this case can readily complete nucleation and then phase separation.

The above results suggest that such a rod can monotonically promote nucleation and a longer one makes nucleation easier.
Fig. 3 (a)–(c) Fraction of particles in the largest cluster $N_i/N$ as a function of time for 30 independent simulation runs. $F_a$ is fixed at 15, and $L$ varies from 4 to 10. (d) Logarithmic mean nucleation time $\ln\langle \tau \rangle$ as a function of $L$. Three activities $F_a = 10, 15$ and 20 are considered. Solid lines are linear fits.

Here we give a qualitative understanding of these findings. It was reported previously that the existence of a boundary can stop the motion of an active particle until it can re-orientate and escape from the boundary. Therefore active particles would accumulate near the boundary (here the rod) and form a small cluster which serves as the initial nucleus and facilitates nucleation. If mapping this active colloidal system far from equilibrium to a passive counterpart, the rare nucleation event in the homogeneous case can be related to an effective free energy barrier $\Delta G$ which is assumed here to be independent of $L$ and the nucleation time scales as $\langle \tau \rangle \sim \exp(\Delta G/k_BT)$. With the introduction of the rod, the accumulation of ABPs near the rod would reduce $\Delta G$ by an amount $\Delta F$. As a rough approximation, one expects that $\Delta F$ would be proportional to the rod length $L$, since a longer rod can offer more nucleation sites, such that $\Delta F = hL$, where $h$ is a constant (may be dependent on $F_a$) and $\langle \tau \rangle \sim \exp[(\Delta G - hL)/k_BT]$. As a result, one can obtain $\ln\langle \tau \rangle \sim zL$ with $z = -h/k_BT$. Indeed, in Fig. 3(d), $\ln\langle \tau \rangle$ decreases with $L$ and has good linear fits with $L$ for all three activities (i.e., $F_a = 10, 15$ and 20) considered, and the coefficients $z$ locate in a relatively narrow range. Furthermore, it can be seen that $\langle \tau \rangle$ increases with $F_a$ for a fixed $L$, which seems to suggest that a higher activity would make nucleation harder.

3. Detachment between the seed and dense phase

One might notice an interesting phenomenon in Fig. 2(b) where the seed detaches from the dense phase after the completion of phase separation. That means that such a rod-like seed can be reused for a possible ‘assembly line’ and would not stay inside the generated cluster as an impurity. In Fig. 4(a), the detachment process of the seed from the dense phase is shown. The orange curve describes the fraction of particles in the largest cluster with the definition used in Fig. 2(d), while the green curve as a comparison describes the fraction of particles in the cluster containing the rod. Clearly, the system first undergoes a nucleation period where active particles try to attach on the rod to form an initial nucleus as shown in the left inset of Fig. 4(a). After that the nucleus grows into a big cluster, which subsequently leads to a dense phase (middle inset). Up to now, the rod is completely surrounded by ABPs and embedded in the dense phase, and thus these two curves in Fig. 4(a) strictly superpose. However the rod would not stay inside the dense phase permanently, but slowly moves to the boundary and finally detaches from it (right inset), as shown by the abrupt decrease of the green curve.

Note that such a non-trivial detachment from the dense phase actually has been reported in a passive colloidal system. In previous theoretical work, A. Cacciuto et al. found that a spherical seed with a smooth surface can induce an initial nucleus with specific size which would detach from the seed later, and then such a seed again becomes free to produce a new crystal – it can therefore act as an ‘assembly line’ for crystal nuclei. Subsequently E. Allahyarov et al. observed this phenomenon in a real colloidal system where the seed favors crystallization only during the initial growth. They found that this is due to the structural incompatibility and curvature between the seed’s surface and the formed crystals, which would lead to the accumulation of elastic distortion with the growth of the crystal, which finally breaks up the connection between them. The elastic distortion would disappear as the curvature tends to zero, and thus colloidal nucleation on a flat wall or substrate would not show such a detachment behavior in passive systems. However, the seed used in the present

Fig. 4 Detachment of the rod from the dense phase. (a) Fraction of particles in the largest cluster $N_i/N$ (orange curve) and of particles in the cluster containing the rod (green curve), as a function of time. The three insets correspond to the three typical stages indicated by the black arrows, where the positions of the rod are highlighted by yellow bars. (b) $N_i/N$ (blue curve) and fraction of orange particles in the dense phase (black curve) as a function of time (see the text). The left inset shows the initial state where particles in the dense phase and dilute phase are colored orange and green, respectively, and the right inset shows the final state. (c) Time cost of the rod detaching from the dense phase $\tau_d$ (green dots), of nucleation $\tau$ (orange dots) and of the rod’s diffusion $\tau_d$ inside the dense phase (blue dots) as a function of rod length. Lines are drawn to guide the eye.
work is a connected-bead rod with zero curvature, but it results in detachment behavior which occurs after the completion of the growth of the cluster instead of in the initial growth stage, suggesting an underlying distinct mechanism in such an active system.

The observed movement of the rod in the dense phase indicates the highly living character of the largest cluster. To confirm this, we initialize the system as a phase-separated state as shown in the left inset of Fig. 4(b), and color the particles in the dense phase as orange and the ones in the dilute phase as green. Then the living character is depicted by analyzing the fraction of particles in the dense phase $N_d/N$ and meanwhile the fraction of orange particles in the dense phase $f$. As can be seen, $N_d/N$ begins from 0.6 and fluctuates slightly around this value, indicating that the system maintains a phase-separated state during the whole time range. Meanwhile $f$ starts from 1.0 and decreases to a steady value about 0.6 equaling $N_d/N$. In the final stage, as shown in the right inset of Fig. 4(b), green particles from the original dilute phase mix fully with orange particles from the dense phase, indicating that the dense phase is highly dynamic and particles even in the innermost region can still move outside to the dilute phase. Therefore, after the completion of phase separation, the seed would slowly diffuse inside the dense phase. As it moves to the boundary of the two phases, the density difference of these two phases would generate a net force that further pushes it away. Once it is in the dilute phase, it can hardly induce nucleation again due to a very low density of ABPs and finally it would wander in the dilute phase permanently. As a comparison, we have further studied the system’s dynamic behaviors with the rod fixed, like the case occurring in previous work, and found that such a rod can hardly detach from the formed dense phase (data are not shown here for simplicity). This can be understood by the fact that the diffusion of such a huge cluster (dense phase) is extremely difficult compared to that of a free rod; even for a transient detachment, a fixed rod would not be pushed away by the density difference between the dilute and dense phase and thus it can quickly connect with the dense phase again.

To further depict quantitatively such a detachment behavior, in Fig. 4(c) we study the total time cost $t$ before the seed detaches from the dense phase. Interestingly, $t$ varies non-monotonically with the rod length $L$ and it has a minimum at a middle size of $L$. Note that $t$ can be divided into two parts: one for nucleation $t_n$ and another one $t_d$ for diffusion inside the dense phase. As confirmed above, $t_n$ decreases with $L$. Meanwhile $t_d$ increases with $L$ because a longer rod can encounter more resistance in the dense phase. Thus these two factors result in a minimum of $t$ that facilitates the detachment most.

4. Effect of the activity on nucleation

We next study the effect of the activity on such heterogeneous active systems. In Fig. 5, the final stationary states of the system with seed size $L = 14$ for $F_a = 5$, 40 and 65 are shown. As can be seen, systems with both low activity $F_a = 5$ (Fig. 5(a)) and high activity $F_a = 65$ (Fig. 5(c)) are single-phase states although the seed indeed induces a small cluster wrapping it as shown in the insets. Meanwhile for $F_a = 40$, interestingly, the system apparently phase separates into a dilute phase and a dense phase. That is, the phase behavior is re-entrant with the activity in such a heterogeneous system.

To understand this novel phase behavior, one can study the origin of phase separation, i.e., the nucleation process, which can be depicted by the change of $N_d/N$. In Fig. 6(a)–(c), $N_d/N$ as a function of time for 30 independent runs is shown, corresponding to $F_a = 10$, 40 and 65, respectively. A complete phase diagram of ABPs in terms of $N_d/N$ to check if the system reaches the steady state or not can be seen in ref. A higher activity makes nucleation harder. Further evidence occurs in Fig. 6(c) corresponding to an even higher activity $F_a = 65$, where all curves of $N_d/N$ directly increase to a stable value from the beginning except a few experience very short inductions, which means that the systems in this case can readily phase separate. Further increasing $F_a$ to 40 (Fig. 6(b)), the curves of $N_d/N$ have to experience obvious induction stages before reaching a plateau at about 0.73. Although such a plateau suggests that the system can still phase separate as shown in Fig. 5(b), the observed long induction period indicates that a higher activity makes nucleation harder. Further evidence occurs in Fig. 6(c) corresponding to an even higher activity $F_a = 65$, where all curves of $N_d/N$ locate at the bottom near zero, corresponding to a single-phase state as shown in Fig. 5(c). To see more directly how the activity affects nucleation, we show the relation between $N_d/N$ and $F_a$ in Fig. 6(d). As can be seen, $N_d/N$ increases with $F_a$ at all considered rod lengths, i.e., $L = 10, 14$ and 20. For a given activity, $N_d/N$ decreases with $L$, which is consistent with the result shown in Fig. 3.

At first glance, the re-entrant phase separation with the activity mentioned above seems in contrast to the general understanding that a higher activity can facilitate phase separation better. For example, if following the general understanding, the system with $F_a = 65$ and $L = 14$ should be phase separated into two phases instead of the observed single phase (Fig. 5(c)). As a comparison, we have also investigated the phase behavior of homogeneous systems with the same parameters as in Fig. 5(b) and (c), i.e., $F_a = 40$ and 65, and observed single-phase states beginning from random initial states of both these two cases. However on introducing a rod ($L = 14$ here) to the system with $F_a = 40$, a phase separated state occurs (Fig. 5(b)), suggesting the observed state in the homogeneous system is a
meta-stable state with a high nucleation barrier and such a rod reduces the barrier and makes \( \langle \tau \rangle \) reachable. Similarly, the single-phase state in the homogeneous system with \( F_a = 65 \) would be also meta-stable. Even on introducing a rod, such a system is still a single-phase state (Fig. 5(c)), which means that the barrier is still high after reduction. To further reduce the barrier and make \( \langle \tau \rangle \) reachable, a longer rod is needed, e.g., \( L = 20 \), and then \( \langle \tau \rangle \) can be reduced to about 230 according to Fig. 6(d), which can be readily reached in the present simulation scope, and a phase-separated state can be indeed observed as the general understanding predicts. That is, the observed re-entrant phase separation doesn’t indicate that the single-phase state is ‘thermodynamically’ stable for large activity \( F_a = 65 \). Rather, it is a meta-stable and sudden and the steady state (phase-separated state) can’t be reached in a finite time scale due to an increasing nucleation barrier with activity. For real experiments and simulations, observations are made in finite time, and thus the re-entrant behavior reported here would be relevant.

The above results suggest that high activity would make nucleation hard and thus suppress phase separation. Here we try to give a qualitative understanding of this finding. In Fig. 7(a), \( N_c/N \) as a function of time is shown accompanied by three insets showing failed nucleation events. During the whole time range, \( N_c/N \) almost keeps a very low value near zero except it has a peak of about 0.15 at \( t \approx 200 \). These three insets depict the system’s states at the moments just before, at and after \( t = 200 \), respectively. As can be seen in the left inset, a small collection of ABPs wraps the rod and forms a small cluster (nucleus), and \( N_c/N \) reaches a peak. Then such a cluster becomes unstable and suddenly rotates by a large angle (middle inset). After that, the ABPs attached to the rod slip away in two opposite directions along the rod (right inset) and the just-formed cluster is broken. Therefore the rotation of the rod could be relevant to the instability of initial nuclei. To further quantitatively describe the rotation, we investigate the rotational diffusion behavior of this rod. In Fig. 7(b), the mean angle square displacements (MASDs) calculated via \( \langle \delta \theta_R^2(t) \rangle = \langle \theta_R(t) - \theta_R(0) \rangle^2 \) for three different values of the activity are shown. Besides, the inset in Fig. 7(b) gives the double logarithmic form of the MASD, wherein the curves show some features which are common for diffusion of passive objects in an active suspension, namely super-diffusion at short time followed by normal diffusion at very long time, corresponding to \( \text{MASD} \sim t^\beta (\beta > 1) \) and \( \text{MASD} \sim t \), respectively. Clearly, the MASD at a higher activity, e.g. \( F_a = 75 \), is larger than that at a lower one, indicating that the rod in an active suspension with higher activity can rotate faster. A more direct presentation of diffusion is shown in Fig. 7(c), which depicts the long time rotational diffusion constant \( D_t \) as a function of \( F_a \). As can be seen, \( D_t \) increases with \( F_a \) for all three rod lengths considered (i.e. \( L = 8 \), 10 and 12), and \( D_t \) decreases with \( L \) for fixed activity. That is, a higher \( F_a \) leads to faster rotation of the rod, which destabilizes the initial nuclei, thus makes nucleation harder and finally suppresses phase separation. As extending \( L \) can slow down the rod’s rotation, the nucleation at a longer rod seeding is shown to be easier and \( \langle \tau \rangle \) is shorter, which is consistent with the results in Fig. 6(d).

### IV. Conclusion

In summary, we have theoretically studied the heterogeneous nucleation process in an active suspension by introducing a
rod-like seed. The active system considered in the present work is so dilute that spontaneous phase separation can be hardly observed in a homogeneous case due to the existing high nucleation barrier. Meanwhile if seeding a rod, such a heterogeneous system can readily phase separate into a dilute and a dense phase, and the nucleation time $t$ decreases exponentially with rod length $L$. We found that the seed would detach from the dense phase after the completion of phase separation, which is reminiscent of a passive colloidal system where the formed crystal would also disconnect from the seed. This novel dynamic behavior could have great prospects in industry, for example the purification of crystals and the construction of an assembly line with a reproducible seed.

We have further investigated the effects of activity $F_a$ on the heterogeneous systems. Interestingly, we found that the phase behavior is re-entrant with $F_a$ in that the system can only phase separate at a moderate $F_a$ while it maintains a single-phase state at both low and high $F_a$. Such a counterintuitive phase behavior seems to disobey the general understanding that a higher activity can promote phase separation better. However subsequent results indicate that a high $F_a$ would lead to a high nucleation barrier and suppress nucleation, and thus the observed single-phase state is actually a meta-stable state instead of a steady state which should be phase separated.

Conflicts of interest
There are no conflicts to declare.

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References