Anomalous Diffusion of Active Brownian Particles in Crystalline Phases

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Abstract. By performing a molecular-dynamics model of active Brownian particles in 2D geometry and systematically changing the system densities, an investigation of the diffusion of active Brownian particles from homogeneous fluid phases to hexagonal-packed crystalline phases is presented. It is found that particle diffusion is short-time superdiffusive and long-time Fickian, where the effective diffusion coefficient decreases with the increasing density. Such behavior can be theoretically captured by a modified overdamped Langevin equation. On the other hand, the displacement distribution of active Brownian particles in dilute suspensions is identified to be governed by the classic diffusion equation. However, dynamic heterogeneity emerges for the fluctuations of systems in crystalline phases, where the tail of van Hove function is found to follow the exponential distribution instead of the Gaussian form. Such anomalous phenomena perhaps could be attributed to the dense environments where the distribution of particle diffusivity is non-uniform. Our findings potentially provide a significant advance in revealing the fundamental nonequilibrium physics of active matter systems.

1. Introduction
Physical systems far from equilibrium have been received an unprecedented growth of attentions regarding the statistical mechanics in the past few years[1]. In particular, active matter systems, where the individual units gain kinetic energy from their surroundings, have been extensively investigated theoretically and experimentally. A rich variety of intriguing non-equilibrium phenomena have been observed in active matter systems, such as targeted delivery[2], unidirectional motors [3] and violation of the fluctuation-dissipation theorem[4]. When numerous active particles act together, collective modes of migration can emerge. Already without adhesive interactions and in the absence of alignment mechanisms, clusters of active particles can form in high-density systems. These clusters appear when there is no interaction that aligns the migration directions of different particles so that they can mutually block their motion. Particularly, when the systems are confined in a two-dimensional (2D) or quasi-2D geometries, these particles can spontaneously form into hexagonal-packed living crystals [5], which cannot be observed in conventional equilibrium systems unless there are strong attractive interactions among these particles.

These phenomena demonstrate that the underlying physics of active matter cannot be governed by the classic physical descriptions. However, an in-depth insight into the corresponding active-matter physics is still lacking. Therefore, to rationalize these behaviors intuitively, active Brownian particles, a stochastic dynamic model describing the motion of interacting active particles based on Brownian dynamics, has been proposed in recent years. This stochastic model has been successfully applied to reproducing these counterintuitive behaviors, corroborating that such model indeed captures the physical essence of active particle systems. Hence, in this paper, active-Brownian-particle model is utilized to explore the inner fluctuations of active matters by investigating the diffusion of active
particles in crystalline phases, which could potentially provide a significant advance in the development of non-equilibrium statistical physics.

2. Model

The minimal model for active Brownian particles [7] is employed by computer simulations, where the suspension consists of $N$ repulsive active disks in a 2D box $L \times L$ with periodic boundary conditions in all directions. The motion of the $i$th active particle with position $r_i$ is governed by the overdamped Langevin equation

$$\dot{r}_i(t) = \frac{D_0}{k_B T} [-\nabla_i U(t) + \xi_i(t) + f \hat{e}_i(t)]$$

(1)

due to the low Reynolds number, where the potential energy $U$ is the sum of interactions between all particle pairs, and $D_0$ is the intrinsic diffusion coefficient. The Gaussian white noise, $\xi_i(t)$, which describes the collisions with the solvent molecules, satisfies $\langle \xi_i(t) \xi_j(t') \rangle = 2(k_B T)^2 \delta_{ij} \delta(t - t')/D_0$ with $\delta$ the identity matrix. The self-propulsion is described by a constant force $f$ in the particle orientation $\hat{e}_i(t)$, which undergoes free Brownian rotation with a rotational diffusivity $D_r$.

Figure 1. (a) The snapshots of simulation systems at $\phi = 0.360, 0.518, 0.774$ and $1.040$ respectively, where the active Brownian particle is represented by a blue round disk. A phase transition can be clearly identified when increasing the number density $\phi$, from a homogeneous fluid to an ordered crystalline state. (b) Corresponding particle trajectories at $\phi = 0.360, 0.518, 0.774$ and $1.040$ respectively. It can be found that the particle motion is free at low $\phi$, but are significantly suppressed in the crystalline phase.

In addition, the pair potential between particle is modeled by the well-known truncated Weeks-Chandler-Andersen (WCA) potential, which is given by

$$U(r) = \begin{cases} 
4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 + \varepsilon & \text{for } r \leq 2^{1/6}\sigma \\
0 & \text{for } r > 2^{1/6}\sigma
\end{cases}$$

(2)

Here, $\sigma$ is the diameter of a self-propelled particle and $r$ is the center-to-center distance between two particles. In our works, the potential strength $\varepsilon$ is set as $1000 k_B T$ to mimic the hard-sphere interactions. Other simulation parameters are $L = 50 \sigma$, $D_0 = 0.01 \sigma^2/\tau$, $D_r = 0.25 / \tau$, where $\tau$ is the time unit in simulations. The constant force $f$ is set as $f = 1000 k_B T/\sigma$ to ensure the formation of living crystals, which means the intrinsic velocity of an active Brownian particle is $v_0 = 10 \sigma/\tau$. 

3. Results and Discussions

\( \phi = N \sigma^2 / L^2 \) is defined as the number density of the system, and use \( \phi \) as the parameter to characterize the states of active Brownian particles. Series of computer simulations are performed by systematically changing the density \( \phi \). As shown by the snapshots in Fig. 1(a), active Brownian particles are identified to be in various states at different \( \phi \). A transition of the system can be observed, from a initially disordered and homogeneous fluid into an ordered and hexagonal-packed state as increasing the number density. The ordered state is comprised of several hexagonal-packed clusters surrounded by a dilute phase of single self-propelled particles. In our simulations, these clusters can finally merge into a single big cluster if the simulation time is sufficient long. The “final” cluster is not static but it is constantly changing its shape while particles are exchanged between the cluster and the diluted phase. Alternatively, it has been pointed out that self-propelled particles lacking an alignment rule exhibit collective behavior and form dense dynamical clusters in equilibrium with a gas phase. This behavior arises from a self-trapping mechanism: self-propelled particles with a persistent time and colliding head on, arrest each other owing to the persistence of their orientation. Meanwhile, the motions of particles are also suppressed when \( \phi \) is high, which is clearly demonstrated by the trajectories of individual active particles in Fig. 1(b). These particles move freely in a dilute suspension, but are more likely to be “trapped” in the crystalline phase due to the limited spaces among large clusters.

To give a more quantitative description of such particle motions and gain an in-depth physical insight into the inner fluctuations in crystalline phases, the diffusion behaviors of active Brownian particles at different \( \phi \) is investigated. Averages over 20 independent runs are performed for each \( \phi \). The mean square displacement (MSDs) \( \langle \Delta r^2(t) \rangle \) for a wide range of \( \phi \) are calculated, where \( \langle \cdots \rangle \) denotes the ensemble average. As shown in Fig. 2(a), unlike conventional Brownian diffusion where the MSD is always proportional to time, i.e., \( \langle \Delta r^2(t) \rangle \sim t \), the mean square displacements of active Brownian particles scale as \( t^2 \) at short-time scales, and enter the Fickian regime where the scale is \( \langle \Delta r^2(t) \rangle \sim t \) at long-time scales. On the other hand, a dynamical criterion for the “trap” in crystalline phases is given by the decrease of the long-time diffusion coefficient \( D_{\text{eff}} \) when increasing the density \( \phi \), which is demonstrated in Fig. 2(b). Here \( D_{\text{eff}} \) is defined by the long-time MSD, given by:

\[
D_{\text{eff}} = \lim_{t \to \infty} \frac{\langle \Delta r^2(t) \rangle}{4t} \tag{3}
\]

Such parameter gives a quantitative description of the particle-motion activities. The small value of \( D_{\text{eff}} \) at high \( \phi \) corroborates that the particle diffusion meets a significant suppression in the crystalline phases.
Figure 2. (a) The mean square displacements of active Brownian particles for a wide range of number density \( \phi \). It can be found that the particle motion is short-time superdiffusive and long-time Fickian. (b) The long-time diffusion coefficient \( D_{\text{eff}} \) versus \( \phi \). A decrease of \( D_{\text{eff}} \) with the increasing \( \phi \) can be identified, where the red solid line is the guide to the eye.

To interpret this anomalous diffusion phenomenon, the motions of active Brownian particles are theoretically described based on the modified version of Eq. (1):

\[
V(t) = v(\phi)e(t) + \xi(t)
\]  

(4)

where \( V(t) \) is the instantaneous particle velocity, and \( v(\phi) \) is the ensemble description self-propulsion velocity with density dependence. Hence, the theoretical MSD of active Brownian particle can be given by:

\[
\langle \Delta r^2(t) \rangle = \int_0^t ds (t - s) \langle V(s) \cdot V(0) \rangle
\]  

(5)

where \( \langle V(s) \cdot V(0) \rangle = v^2(\phi)\langle \dot{e}(s) \cdot \dot{e}(0) \rangle + \langle \xi(s) \cdot \xi(0) \rangle = v^2(\phi)e^{-2D_r s} + 4D_0 \delta(s) \) owing to that the correlation of \( \dot{e} \) decays exponentially for Brownian rotations. Therefore,

\[
\langle \Delta r^2(t) \rangle = \frac{v^2(\phi)}{4D_r} (e^{-2D_r t} + 2D_r t - 1) + 4D_0 t
\]  

(6)

by solving the integral in Eq.(5). Thus, for short-time scale \( t \to 0 \), MSD can be expressed as \( \langle \Delta r^2(t) \rangle = v^2(\phi)t^2/2 + 4D_0 t \) based on the Taylor series, i.e., the particle diffusion is short-time superdiffusive. For long-time scale \( t \gg 0 \), MSD can be approximated by \( \langle \Delta r^2(t) \rangle = (v^2(\phi)/2D_r + 4D_0)t \), indicating that the particle motion is long-time Fickian.

Based on Eq. (6), the theoretical \( D_{\text{eff}} \) can be given by:

\[
D_{\text{eff}} = \lim_{t \to \infty} \frac{\langle \Delta r^2(t) \rangle}{4t} = \frac{v^2(\phi)}{8D_r} + D_0
\]  

(7)

where \( v(\phi) \) equals \( v_0 \) in dilute suspension but dramatically decreases in crystalline phases owing to the limited spaces. Thus, the value of \( D_{\text{eff}} \) shows an inevitable drop when increasing the number density \( \phi \).

Next the displacement distribution of active Brownian particles is investigated to explore the heterogeneity of dynamics in active matter systems. The self-part of the van Hove correlation function \( G_s(r,t) = \langle \delta[r - [r(t) - r(0)] \rangle \) is used to characterize such distributions based on equilibrated configurations in our simulations. The displacement distributions for \( \phi = 0.16 \) and \( 0.77/\sigma^2 \) at time
\( t = 0.1 \) and \( 0.5 \tau \) respectively are shown in Fig. 3. In dilute suspensions, the short-time displacement is identified to be Gaussian distributed, following the descriptions of classic Brownian motion which is governed by the Fick’s laws of diffusion, as demonstrated in Fig. 3(a) \((t = 0.1 \tau)\). However, when increasing the time scale [Fig. 3(b) where \( t = 0.5 \tau \)], the van Hove correlation function becomes a symmetric curve with two peaks, indicating that the most probable displacement is shifted due to the self-propulsion of active Brownian particles. On the other hand, as shown in Figs. 3(c) and (d), in the crystalline phases, the displacement distributions of active particles are both one-peak-distributed in dilute and dense suspensions, where the most probable displacements are both zero.

![Figure 3](image_url)

Figure 3. The self-part of the van Hove correlation function \( G_s(r,t) \) at (a) \( \varphi = 0.16/\sigma^2 \) and \( t=0.1\tau \); (b) \( \varphi=0.16/\sigma^2 \) and \( t=0.5\tau \); (c) \( \varphi=0.77/\sigma^2 \) and \( t=0.1\tau \); (d) \( \varphi=0.77/\sigma^2 \) and \( t = 0.5\tau \) respectively. The blue solid lines are obtained by Eq. (10), which show great agreements with the simulation results.

To rationalize these anomalous behaviors intuitively, the one-dimensional (1D) diffusion equation is considered to obtain the analytic van Hove function of active Brownian particles at different time scales. The diffusion equation can be written as:

\[
\frac{\partial G_s(x,t|x_0)}{\partial t} = -v(\varphi) \frac{\partial G_s(x,t|x_0)}{\partial x} + D_0 \frac{\partial^2 G_s(x,t|x_0)}{\partial x^2} \tag{8}
\]

with the initial condition given by \( G_s(x,t=0|x_0) = \delta(x-x_0) \), where \( x(t) \) and \( x_0 \) are the particle positions at time \( t \) and 0 respectively. Considering the Galilean invariance of the system, the initial position of the particle is fixed at the origin of the Cartesian coordinates. Therefore, using the Laplace transform, the analytic solution of Eq. (8) can be easily obtained, given by:

\[
G_s(x,t) = \frac{1}{\sqrt{4\pi D_0 t}} \exp \left( -\frac{[x-v(\varphi)]^2}{4D_0 t} \right) \tag{9}
\]

which follows the Gaussian form with a non-zero mean. For the reason that there is no alignment of self-propulsion for active Brownian particles, there is no preferred direction for the displacement in 2D geometry. Thus, the 2D \( G_s(x,t) \) should be the directional average of 1D van Hove functions. That is, the displacement distributions in 2D geometry can be statistically described by:

\[
G_s(x,t) = \int_0^{2\pi} d\theta G_s(x,t|\theta) = \int_0^{2\pi} d\theta \frac{1}{2\pi \sqrt{4\pi D_0 t}} \exp \left( -\frac{[x-v(\varphi)\cos\theta]^2}{4D_0 t} \right) \tag{10}
\]
where \( v(\phi) \cos \theta \) is the component of intrinsic velocity in \( x \) or \( y \) directions. Such integral has no analytic expression, the numerical value of \( G_s(r, t) \) is used instead in our works below. In Fig. 3 the predicted distributions given by Eq. (10) are shown as solid blue lines, which demonstrate great agreements with the simulation results in small displacement regimes.

However, when examining the tail of van Hove correlation function in crystalline phases, it can be found that the diffusion of active Brownian particles violates the description of classic diffusion equation. Although strictly Fickian behavior was observed in crystalline phases, the tail of displacement distributions shows an exponentially decay instead of the prediction by Eq. (10), which has been clearly shown in Fig. 4 (\( \phi = 0.77 \) and \( t = 0.5\tau \)). In principle, the displacement distribution would revert to Gaussian at sufficiently long times owing to the bound of central limit theorem, but this was not observed. This could be the consequence of that the active matter system relaxation time in crystalline phases so much exceeds the time on which these simulations were conducted. In fact, it was the opposite: The contribution of the central portion that could be fitted by Eq. (10) decreased with the elapsed time. Inspection shows that the crossover point from Gaussian to exponential occurs approximately at the average distance between large clusters, suggesting that dynamic heterogeneity do exist in the inner fluctuations of active Brownian particles.

One physically motivated interpretation of such non-Gaussianity is that , such distribution is described by the convolution of Gaussian, independently diffusive processes. In general speaking, this

![Image](image_url)

Figure 4. Log plot of the self-part of the van Hove correlation function \( G_s(r, t) \) at \( \phi = 0.77/\sigma^2 \) and \( t = 0.5\tau \). The blue dashed lines are obtained by Eq. (10), and red solid lines are the exponential fit to data.

A violation of the description of classic diffusion equation can be found at the tail of \( G_s(r, t) \), indicating that dynamic heterogeneity do exist in the inner fluctuations of active Brownian particles.
is the statistical-mechanics approach of decomposing complex processes into normal modes, and it bears direct relevance to systems with different microscopic origins for the dynamic heterogeneity. Mathematically, such an approach can be described by:

\[ G_g(x, t) = \int P(D) \cdot g(x \mid D) \cdot dD \] (11)

where \( P(D) \) is the effective distribution of diffusivities, which reflects physically the temporal correlation of microscopic fluctuations, and \( g(x \mid D) = 1/\sqrt{4\pi Dt} \exp(-x^2/4Dt) \). For active Brownian particles in crystalline phases, the limited spaces among large clusters could lead to a non-uniform distribution of diffusivities. Therefore, \( G_g(x, t) \) can be approximated by a steepest descent analysis to:

\[ G_g(x, t) \approx \int \frac{dD}{\sqrt{D}} \cdot e^{\ln(P(D)) - x^2/4Dt} \] (12)

In the limit of constant \( \partial \ln(P(D))/\partial D \), \( G_g(x, t) \) is exponential whereas it is closer to Gaussian when \( \partial \ln(P(D))/\partial D \) is a strong function of \( D \). In physical terms, the more heterogeneous the dynamics is in regimes of large amplitude, the closer to exponential the displacement distributions are anticipated to be. Such phenomena also indicate that the fluctuations in the system of active Brownian particles should be colored, that is, the system noise has unevenly distributed frequencies - such as proteins diffusing on lipid membranes with power-law fluctuations. That is why the tail of van Hove function is exponentially distributed for particles in crystalline phases where the dynamics could be much heterogeneous.

4. Conclusion
In summary, by performing a molecular-dynamics model of active Brownian particles in 2D geometry, an investigation of the diffusion of active Brownian particles from homogeneous fluid phases to hexagonal-packed crystalline phases is presented by systematically changing the system densities. By examining the mean square displacements of particles, it is found that the particle diffusion is short-time superdiffusive and long-time Fickian, where the effective diffusion coefficient decreases with the increasing system density. Such behavior can be theoretically captured by a modified overdamped Langevin equation. On the other hand, the displacement distribution of active Brownian particles in dilute suspensions is identified to be governed by the classic diffusion equation. However, dynamic heterogeneity emerges for the fluctuations of systems in crystalline phases, where the tail of van Hove function is found to be exponentially distributed. Such anomalous phenomena perhaps could be attributed to the dense environments where the distribution of particle diffusivity is non-uniform. Our findings potentially provide a significant advance in revealing the fundamental nonequilibrium physics of active matter systems.

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