

Phoretic self-assembly of active colloidal molecules

Lijie Lei(雷李杰), Shuo Wang(王硕), Xinyuan Zhang(张昕源), Wenjie Lai(赖文杰), Jinyu Wu(吴晋宇), Yongxiang Gao(高永祥)

Citation: Chin. Phys. B, 2021, 30 (**5**): 056112. DOI: 10.1088/1674-1056/abc2bd
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Continuous-wave operation of InAs/InP quantum dot tunable external-cavity laser grown by metal-organic chemical vapor deposition

Yan Wang(王岩), Shuai Luo(罗帅), Haiming Ji(季海铭), Di Qu(曲迪), and Yidong Huang(黄翊东)
Chin. Phys. B, 2021, 30 (**1**): 018106. DOI: 10.1088/1674-1056/abcfa4

Fluorescence spectra of colloidal self-assembled CdSe nano-wire on substrate of porous Al_2O_3/Au nanoparticles

Xin Zhang(张欣), Li-Ping Shao(邵丽萍), Man Peng(彭嫚), Zhong-Chen Bai(白忠臣), Zheng-Ping Zhang(张正平), Shui-Jie Qin(秦水介)
Chin. Phys. B, 2019, 28 (**6**): 068103. DOI: 10.1088/1674-1056/28/6/068103

Effect of substrate type on Ni self-assembly process

Xuzhao Chai(柴旭朝), Boyang Qu(瞿博阳), Yuechao Jiao(焦岳超), Ping Liu(刘萍), Yanxia Ma(马彦霞), Fengge Wang(王凤歌), Xiaoquan Li(李晓荃), Xiangqian Fang(方向前), Ping Han(韩平), Rong Zhang(张荣)
Chin. Phys. B, 2019, 28 (**1**): 016102. DOI: 10.1088/1674-1056/28/1/016102

Photoelectric characteristics of silicon P-N junction with nanopillar texture：Analysis of X-ray photoelectron spectroscopy

Liu Jing, Wang Jia-Ou, Yi Fu-Ting, Wu Rui, Zhang Nian, Ibrahim Kurash
Chin. Phys. B, 2014, 23 (**9**): 096101. DOI: 10.1088/1674-1056/23/9/096101

Band structure characteristics of T-square fractal phononic crystals

Liu Xiao-Jian, Fan You-Hua
Chin. Phys. B, 2013, 22 (**3**): 036101. DOI: 10.1088/1674-1056/22/3/036101

SPECIAL TOPIC — Active matters physics

Phoretic self-assembly of active colloidal molecules*

Lijie Lei(雷李杰)[1,2], Shuo Wang(王硕)[1,2], Xinyuan Zhang(张昕源)[1], Wenjie Lai(赖文杰)[1], Jinyu Wu(吴晋宇)[1], and Yongxiang Gao(高永祥)[1,†]

[1] *Institute for Advanced Study, Shenzhen University, Shenzhen* 518060, *China*
[2] *Institute of Microscale Optoelectronics, Shenzhen University, Shenzhen* 518060, *China*

(Received 18 August 2020; revised manuscript received 14 September 2020; accepted manuscript online 20 October 2020)

We simulate the self-assembly of active colloidal molecules from binary mixtures of spherical particles using a Brownian dynamics algorithm. These particles interact via phoretic interactions, which are determined by two independently tunable parameters, surface activity and surface mobility. In systems composed of equal-size particles, we observe the formation of colloidal molecules with well-defined coordination numbers and spatial arrangement, which also display distinct dynamic functions, such as resting, translating, and rotating. By changing the size ratio to 2 : 1 between the two species, we further observe the formation of colloidal molecules with new structures arising from breaking the size symmetry. By tuning the mutual interactions between the smaller species via their surface mobility, we are able to control their spacing as well as the coordination number of the colloidal molecules. This study highlights the importance of tuning surface parameters and size asymmetry in controlling the structure and the active dynamics of colloidal molecules.

Keywords: Brownian dynamics, diffusiophoresis, active colloidal molecule, self-assembly

PACS: 82.70.Dd, 61.43.Hv, 81.16.Dn, 83.10.Rs **DOI:** 10.1088/1674-1056/abc2bd

1. Introduction

Colloidal molecules refer to the assembly of colloidal clusters with well-defined coordination number and spatial arrangement.[1] They are often regarded as mesoscopic counterparts of molecules as colloidal particles are several orders of magnitude bigger than atoms.[2] Of particular interest are active colloidal molecules, which contain at least one species that can self-propel or swim.[3] By extracting energy from the environment and convert it into self-propelled motion, active colloidal molecules are able to perform various dynamic functions, such as translation, rotation, and *in-situ* assembly–disassembly with high accuracy.[4–7] Studying the self-assembly process of active molecules is not only beneficial for the design and fabrication of miniaturized machines and devices,[8,9] it also promises insights into understanding how active matter organizes into complex and robust dynamic structures,[10] including collections of motile microorganisms,[11] animal flocks,[12,13] and chemical or mechanical imitations.[14,15]

Diffusiophoresis is known as the migration of colloidal particles in response to an externally imposed solute concentration gradient.[16,17] It is a generic strategy for the design of self-propelled active colloids[18] and nonequilibrium interactions for self-assembly of colloidal molecules.[19] For active colloids, the solute gradients are commonly generated by their catalytic surfaces. Through designing the surface with unbalanced catalytic activity, the chemical reaction will produce an asymmetric concentration field, which interacts with the particle, resulting in self-propelled motion or self-phoresis.[20–23] Asymmetric catalytic activity on colloids' surface has been widely used to produce self-propelled Janus colloids in hydrogen peroxide[24] and other chemicals.[25–27]

Diffusiophoretic motion fundamentally relies on two distinct physicochemical properties of the colloids. The first one is the surface activity, which refers to the colloid's ability to generate or consume solute molecules through chemical reactions at their surface.[20] The second one is surface mobility, also termed as phoretic mobility,[16] which leads to an effective slip motion of the colloid in response to gradients in surface concentration. The collective propulsion and rotation of the colloidal molecules are intimately linked to their exact geometry.

In this work, we simulate the self-assembly of active colloidal molecules in binary systems in which colloidal particles interact and respond via diffusiophoresis. Our aim is to investigate the influence of surface parameters and size asymmetry on the structure and dynamics of active colloidal molecules. Note that phoretic interactions between particles are not restricted to be reciprocal and are inherently nonequilibrium, which therefore may lead to self-assembled structures and dynamic functions that are unseen in colloidal self-assembly driven by thermodynamics.

*Project supported by the Innovation Program of Guangdong Provincial Department of Education, China (Grant No. 2019KTSCX148) and the Science and Technology Innovation Commission of Shenzhen (Grant No. JCYJ20170818141727254).

†Corresponding author. E-mail: yongxiang.gao@szu.edu.cn

© 2021 Chinese Physical Society and IOP Publishing Ltd

2. Model and methodology

There are two independent parameters to characterize the properties of spherical catalytic colloids,[19] which are surface activity (α) and surface mobility (μ). Both the surface activity and surface mobility can be positive or negative (or even zero). Experimentally, these two parameters can be manipulated by modifying the surface chemistry of colloidal particles.

Specifically, the concentration field $C(r)$ around a catalytic particle in 3D can be obtained by solving the diffusion equation

$$\nabla^2 C = 0, \tag{1}$$

with a boundary condition

$$-D\frac{\partial C}{\partial r}|_{r=R}=\alpha, \tag{2}$$

where D is the diffusion coefficient of the chemicals, R is the radius of the colloidal particle, and α is the surface activity of the particle. The resulted concentration field decays as $1/r$,

$$C(r) \sim \frac{\alpha R^2}{Dr}. \tag{3}$$

Now, consider two colloidal particles with radius (R_1, R_2), surface activity (α_1, α_2), and surface mobility (μ_1, μ_2), respectively that are in each other's concentration field. Here we ignore the hydrodynamic interaction between the particles and assume that the concentration field will not be disturbed by the presence of other particles. Within the far-field approximation, the drift velocity of particle 2 in the concentration field produced by particle 1 can be described as

$$\boldsymbol{V}_2 = -\mu_2 \nabla C|_1 \sim \alpha_1\mu_2\left(\frac{R_1^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right), \tag{4}$$

in which $\boldsymbol{r}_{12}=\boldsymbol{r}_2-\boldsymbol{r}_1$, and $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$ are the vectors describing the positions of particles 1 and 2, respectively. Similarly, the drift velocity of particle 1 in the concentration field produced by particle 2 can be obtained as

$$\boldsymbol{V}_1 = -\mu_1 \nabla C|_2 \sim -\alpha_2\mu_1\left(\frac{R_2^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right). \tag{5}$$

We should note that $\boldsymbol{V}_1 \neq -\boldsymbol{V}_2$ in general because $\alpha_1\mu_2 \neq \alpha_2\mu_1$ even when the two particles are of equal size, $R_1 = R_2$. This implies a broken action-reaction symmetry for interspecies interactions. The fact that the action-reaction symmetry is broken indicates that the whole pair moves with a velocity

$$\boldsymbol{V}_{\text{propel}} \sim \alpha_1\mu_2\left(\frac{R_1^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right) - \alpha_2\mu_1\left(\frac{R_2^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right). \tag{6}$$

2.1. Binary system composed of colloidal particles of equal size

As pointed out by Soto and Golestanian,[19] the effective interaction between phoretic colloids is similar to the unscreened electrostatic interaction between charged colloids in a fluid. The sign of the interaction, being repulsive or attractive, depends only on the signs of the surface parameters (α, μ) , which are summarized in Table 1. The first term and the second term in the table refer to the interaction applied to particle 1 induced by particle 2 and the interaction applied to particle 2 induced by particle 1, respectively. It becomes obvious that when the product of $\alpha_1\mu_2$ is less than zero, particle 2 will be attracted by particle 1. On the contrary, when the product of $\alpha_1\mu_2$ is greater than zero, the particle 2 will be repelled by particle 1. $\alpha_2\mu_1$ describes the interaction of particle 1 induced by particle 2 in the same way. Table 1 highlights the richness in the pair interactions of binary systems based on the current diffusiophoresis model, which can be tuned by adjusting the surface parameters to realize a wealth of self-assembled structures and dynamic functions. If the interaction is attractive for two particles, it is possible to form a most basic colloidal molecule, i.e., a dimer. The whole pair will move with a velocity proportional to $\alpha_1\mu_2-\alpha_2\mu_1$, while the two colloids attract each other with a relative velocity proportional to $\alpha_1\mu_2+\alpha_2\mu_1$.[19]

Table 1. Interaction pattern between active colloids (R: repulsive, A: attractive).

α_2,μ_2 \ α_1,μ_1	+, +	+, −	−, +	−, −
+, +	R, R	R, A	A, R	A, A
+, −	A, R	A, A	R, R	R, A
−, +	R, A	R, R	A, A	A, R
−, −	A, A	A, R	R, A	R, R

2.2. Binary system composed of colloidal particles of different size

A mixture of colloidal particles with the same surface parameters but different size will break the geometry symmetry, which will lead to the formation of moving colloidal molecule or even flocking. Consider a dimer composed of two particles with the same surface activity $\alpha_1=\alpha_2=\alpha^*$ and surface mobility $\mu_1=\mu_2=\mu^*$ but different radii R_0 and R. The whole pair velocity is proportional to the sum of each particle analogous to Eq. (6), so we can have

$$\begin{aligned}\boldsymbol{V}_{\text{propel}} &\sim \alpha_1\mu_2\left(\frac{R_0^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right) - \alpha_2\mu_1\left(\frac{R^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\right)\\ &= \alpha^*\mu^*\frac{R_0^2\boldsymbol{r}_{12}}{D|\boldsymbol{r}_{12}|^3}\left(1-\frac{R^2}{R_0^2}\right).\end{aligned} \tag{7}$$

As can be seen, when $R = R_0$, the two particles have the same radius, the velocity of the pair will be zero, due to the action-reaction symmetry. When $R \neq R_0$, the symmetry is broken, resulting in self-propelled motion of the dimer.

2.3. Equation of motion

The equation of motion governing the behaviors of colloidal particles based on the current model have been described previously,[19] which is the following stochastic equa-

tion:

$$\frac{\mathrm{d}\boldsymbol{r}_i}{\mathrm{d}t} = \sum_{j\neq i}\frac{\alpha_j\mu_i R_j^2}{6\pi D}\frac{\boldsymbol{r}_{ji}}{|\boldsymbol{r}_{ji}|^3}+\boldsymbol{\xi}_i(t)$$
$$= V_0\sum_j \hat{\alpha}_j\hat{\mu}_i\frac{\sigma_j^2\boldsymbol{r}_{ji}}{|\boldsymbol{r}_{ji}|^3}+\boldsymbol{\xi}_i(t), \quad (8)$$

in which $\boldsymbol{r}_i$ is the position of the i-th colloidal particle and $V_0=\frac{\alpha_0\mu_0 R_k^2}{6\pi D\sigma_k^2}=\frac{\alpha_0\mu_0}{24\pi D}$ is the overall velocity scale. σ_j is the radius of colloidal particle j. Use α_0 and μ_0 as characteristic values of the surface chemistry and surface mobility. The dimensionless surface chemical and dimensionless surface mobility are defined as activity $\tilde{\alpha}=\alpha/\alpha_0$ and $\tilde{\mu}=\mu/\mu_0$, respectively. The first term depicts the phoretic interactions of colloidal particles i and j in the far-field approximation and $\boldsymbol{\xi}_i(t)$ is a random velocity applied to particle i at time t, representing white noise with intensity D_c which is proportional to $k_\mathrm{B}T$. The dimensionless white noise intensity is further defined as $\tilde{D}_\mathrm{c}=D_\mathrm{c}/V_0\sigma$.

In general, colloidal particles in experiments cannot overlap. In our simulation, to impose the exclude volume effect, two particles are reflected by the same overlapping distance if they start to overlap. The procedure is repeated until there are no remaining overlaps. Periodic boundary conditions are used, and the interactions are treated using the minimal image convention.[28,29] As most of the experiments are confined to 2D, we confine the colloidal particles to a quasi-3D domain by limiting the center of the particle to move within half of the particle's radius without considering real plates to avoid additional complexity. When the particles reach this imaginary boundary, they are bounced forward to the domain. This allows us to apply the formulas derived for three-dimensional systems to this quasi-3D condition.

3. Results and discussion

In the current system, the area fraction ϕ is defined as $\phi=N\pi\sigma^2/4L^2$, where N is the total number of colloidal particles used in the simulation, and L is the length of our squared domain. The overall velocity scale used in the current systems is $V_0=100.0$ and the white noise magnitude $D_\mathrm{c}=1.0$. The system is advanced in a time step of $\delta t=0.001\sigma/V_0$. The diffusiophoresis interaction is truncated at $r=20R$, beyond which the concentration gradient has decayed low enough to be overlooked.

3.1. Binary systems with colloidal particles of equal size

We first simulate the behaviors of binary system composed of equal-size colloidal particles (species A and B) with different surface activity (α_A,α_B) and surface mobility (μ_A,μ_B), respectively. The simulation is performed with $N=20$ and $L=20$ with mono-dispersed colloidal particle's radius $R=0.5$, resulting in an area fraction $\phi=0.98\%$. Initially the colloidal particles were randomly distributed in the box. The simulation runs up to 1 million steps to allow the colloids to form colloidal molecules and achieve active behaviors. Because of the nonequilibrium property of the current system, it is possible to manipulate the surface parameters to obtain stable colloidal molecules with different configurations and dynamic functions.

Figure 1 presents the formed active colloidal molecules that display translational dynamic functions. The dynamic processes of forming these active colloidal molecules are shown in movie S1. In these configurations, the colloidal molecules will move upwards. This is due to the fact that the active colloidal particle (red) generates a concentration gradient that attracts the passive colloidal particles (blue) to move towards it with a velocity of $\boldsymbol{V}_B\sim\tilde{\alpha}_A\tilde{\mu}_B\left(\frac{R_A^2\boldsymbol{r}_{AB}}{D|\boldsymbol{r}_{AB}|^3}\right)$. Similarly, the velocity of the red particle is $\boldsymbol{V}_A\sim-\tilde{\alpha}_B\tilde{\mu}_A\left(\frac{R_B^2\boldsymbol{r}_{AB}}{D|\boldsymbol{r}_{AB}|^3}\right)=0$ in the current cases. For Fig. 1(a), it is quite straightforward that the overall velocity of the molecule is proportional to $\alpha_A\mu_B-\alpha_B\mu_A$ due to its geometry symmetry. The self-propelled direction of colloidal molecules in Figs. 1(b)–1(d) is also upwards, which can be derived by simple velocity vector superposition. Similarly, the overall velocity of these molecules is proportional to $\alpha_A\mu_B-\alpha_B\mu_A$ since for a fixed configuration the surface parameters are the only factors that control the magnitude of the colloids' interaction and propelling velocity.

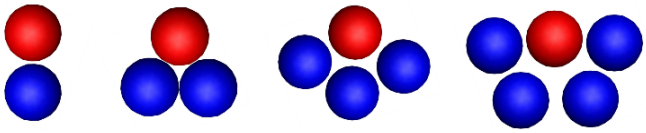


Fig. 1. Configurations of active colloidal molecules AB_n with translational dynamic functions. n varies from 1 to 4 in (a)–(d). Colloid A is red and colloid B is blue, with $\tilde{\alpha}_A=1.0$, $\tilde{\mu}_A=0.0$, $\tilde{\alpha}_B=0.0$, $\tilde{\mu}_B=-1.0$.

In Fig. 2, we present configurations of several colloidal molecules that display dynamic functions of rotation, see movies S2, S3, and S4. Since $\tilde{\alpha}_i\tilde{\mu}_i>0$ and $\tilde{\alpha}_i\tilde{\mu}_j|_{i\neq j}<0$, colloidal particles with the same surface parameters repel each other while the different species of particles attract each other. At the same time, the red particles attract blue particles with a stronger phoretic interaction than the attraction of blue colloids to red colloids since $\tilde{\alpha}_A\tilde{\mu}_B>\tilde{\alpha}_B\tilde{\mu}_A$. These arrangements break the action-reaction symmetry and lead to the rotation of the colloidal molecules.

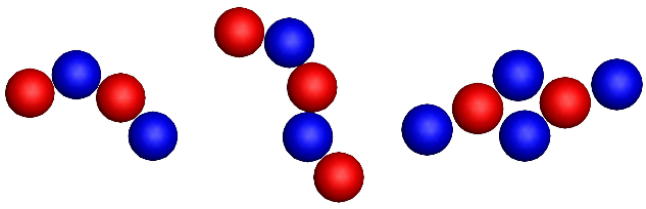


Fig. 2. Configurations of active colloidal molecules with rotational dynamic functions. All the colloidal molecules rotate in clock-wise direction. (a) $\tilde{\alpha}_A=1.0$, $\tilde{\mu}_A=3.0$, $\tilde{\alpha}_B=-1.0$, $\tilde{\mu}_B=-1.0$; (b) and (c) $\tilde{\alpha}_A=2.0$, $\tilde{\mu}_A=1.0$, $\tilde{\alpha}_B=-1.0$, $\tilde{\mu}_B=-1.0$.

In Fig. 3, we present configurations of self-assembled active colloidal molecules that remain rest due to their symmetric structures (the dynamic process of forming these colloidal molecules are shown in movies S5 and S6). Even though Fig. 3(a) has the same configuration with Fig. 1(a), however, the pair velocity parameter $\tilde{\alpha}_A\tilde{\mu}_B - \tilde{\alpha}_B\tilde{\mu}_A = 0.0$ in Fig. 3(a), which results in a rest configuration. Moreover, the interaction between the same species of particles are repulsive in Figs. 3(a), 3(b), 3(f) since $\tilde{\alpha}_i\tilde{\mu}_i = 1 > 0$ while the interaction between particles 1 and 2 is attractive since $\tilde{\alpha}_A\tilde{\mu}_B = \tilde{\alpha}_B\tilde{\mu}_A = -1.0$. Note that the magnitude of the attraction is equal to the repulsion in this case. The *ABAB* chain is formed because among the same species of particles they have a repulsive interaction, leading to the fact that they cannot approach a particle from the same species. On the other hand, there is an attractive interaction between colloidal particles from different species, resulting a configuration *A*–*B*–*A*–*B*. The interaction modes of colloids in Figs. 3(c)–3(e) are similar. However, the magnitudes of attraction and repulsion between the colloids are different. Specifically, the attraction applied on the blue colloids is larger than the repulsion between blue colloids $|\tilde{\alpha}_A\tilde{\mu}_B| > |\tilde{\alpha}_B\tilde{\mu}_B|$, which allows the blue colloids attached to the red colloids, overcoming the repulsion among blue colloids to some extent.

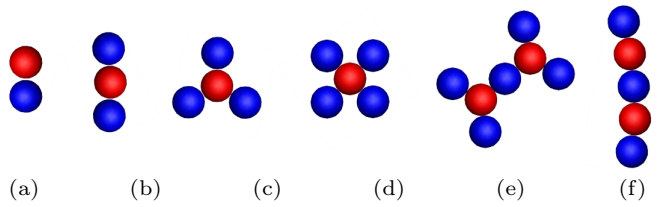


Fig. 3. Configurations of stationary active colloidal molecules of (a) *AB*, (b) AB_2, (c) AB_3, (d) AB_4; (e) A_2B_5, and (f) A_2B_3. For (a), (b), (f) $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 1.0$, $\tilde{\alpha}_B = -1.0$, $\tilde{\mu}_B = -1.0$; for (c), (d), (e) $\tilde{\alpha}_A = 2.0$, $\tilde{\mu}_A = 1.0$, $\tilde{\alpha}_B = -1.0$, $\tilde{\mu}_B = -1.0$.

3.2. Binary systems with colloidal particles of different size

Then we simulate colloidal particles that have the same surface activity and surface mobility with different radii. The previous results have shown that the colloidal particles with the same radius, but different surface parameters may form different colloidal molecules and some of them may move together, which is due to the break of action-reaction symmetry. First the configurations of active colloidal particles with different radii are investigated with a radius ratio $R/R_0 = 0.5$. Figure 5 shows the configurations of colloidal particle formed by colloids with different radius but the same surface parameters, see in movie S7. As analyzed in Eq. (7), different radii of the colloids break the symmetry of geometry, resulting in the translational active colloidal molecules shown in Fig. 4. Since the interactions between all these colloids are attractive only, these colloidal molecules will keep growing when they approach each other. In addition, Fig. 5 presents some other basic configurations of active colloidal molecules formed by colloids with different radii and surface parameters, including one dimer (*AB*), two types of trimers (AB_2 and A_2B), one type of A_3B molecule, one type of AB_3 and one type of A_2B_4 molecules, see movies S8, S9, and S11. Some of the configurations, i.e., (a), (b), and (d), are the same with the colloidal molecules in Fig. 4, but the moving directions are different. In Fig. 4, all the colloidal molecules move with the red colloid leading while in Figs. 5(a) and 5(b) these colloidal molecules move with the blue colloid leading. Compared with the monodispersed cases, there are more spaces for the small colloids to assemble around the big colloids, allowing more compact configurations. Since the colloidal molecules are moving, these molecules will keep growing by attracting nearby colloids, gradually either forming a symmetry molecule or flocking.

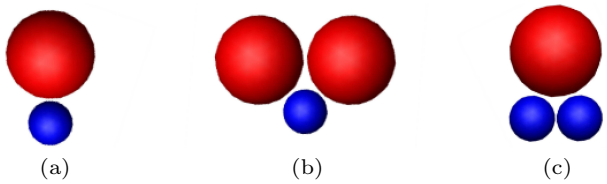


Fig. 4. Colloidal molecules formed by colloids with the same surface parameters but different radius ($\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = -1.0$, $\tilde{\alpha}_B = 1.0$, $\tilde{\mu}_B = -1.0$).

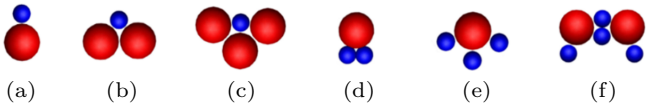


Fig. 5. Basic configurations of active colloidal molecules with different surface parameters (colloid *A* is the big red particles and colloid *B* is the blue particles). For the *AB*, A_2B, and A_3B molecules in (a), (b), and (c) $\tilde{\alpha}_A = 0.0$, $\tilde{\mu}_A = -1.0$, $\tilde{\alpha}_B = 1.0$, $\tilde{\mu}_B = 0.0$; for the AB_2 molecule in (d) $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = 0.0$, $\tilde{\mu}_B = -1.0$; for the AB_3 molecule in (e) $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = -1.0$, $\tilde{\mu}_B = -1.0$, and for the A_2B_3 molecule in (f) $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = -1.0$, $\tilde{\mu}_B = -1.0$.

In addition, due to the size asymmetry of the colloids, it is possible to form AB_n colloidal molecules, a big colloid surrounded by a layer of small colloids. As shown in Fig. 6, the basic diffusiophoresis interaction mode is that the big colloid attracts the small colloids, leading to the small colloids filling all the possible space near the big colloid. The dynamic processes of forming these AB_n colloidal molecules are shown in movies S9, S10, and S11. Specifically, $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = 0.0$, $\tilde{\mu}_B = -1.0$ in Fig. 6(a), which indicates that there is an attractive interaction between the big and small colloids. In this scenario, the small colloids distribute compactly around the big colloid and the big colloid keep attracting small colloids. At the same time the growing colloidal molecule moves with a velocity proportional to $\tilde{\alpha}_A\tilde{\mu}_B - \tilde{\alpha}_B\tilde{\mu}_A$, and keeps attracting the nearby small colloids. Finally, all the nearby space of the big colloid is filled with small colloids, forming a AB_{10} molecule. In addition, altering the radius ratio of the colloids can change the space available for the small colloids to configure around the big colloids, affecting the coordination number of the assembled colloidal molecules. Figure 6(b) plots the

configurations of colloidal molecules with different radius ratios. It is reasonable that with the increase of the radius ratio the coordination number of AB_n molecules will keep decreasing, for $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = -0.0$, $\tilde{\mu}_B = -1.0$, from AB_{10} to AB_4 since bigger colloids will occupy more space around the big red colloid.

Formation of AB_n molecules with different coordination numbers and configurations of the small colloids is possible by tuning the surface parameters such that a weak repulsion is added among the small colloids. In Figs. 6(c) and 6(d), the surface activities of the small colloids are $\tilde{\alpha}_B = -0.5$ and $\tilde{\alpha}_B = -1.0$, respectively. Since $\tilde{\alpha}_B\tilde{\mu}_B > 0$ for these two cases, there will be a repulsion between the small colloids. As can be seen in the figures, similar colloidal molecules are formed compared with Fig. 6(a). However, we can see some obvious difference at the beginning stage of the molecule growth. When the colloidal molecule is still at the AB_2 stage, the small colloids attach to each other if there is no repulsive interaction (Fig. 6(a)). However, the small colloids will stay some distance away from each other as there is a repulsive phoretic interaction between them and form a different bond angle depending on the strength of the repulsion. It is obvious that the stronger the repulsion, the bigger the bond angle. Moreover, because of this bond, the entire colloidal molecule can only further grow into AB_7 and AB_5 with a maximum coordination number of 7 and 5, respectively. Once these symmetric configurations are reached, the active colloidal molecules stop moving. In these cases, the small colloids distribute more evenly around the big colloid in comparison to the case where there is no repulsion between the small colloids. The separation between the small colloids is mainly controlled by the strength of repulsion interaction between these small colloids. As can be seen, $\alpha_B\mu_B = 0.5$ and 1.0 for Figs. 6(c) and 6(d), respectively, indicating a stronger repulsion for small colloids in Fig. 6(c) and leading the small colloids to stay at further separation from each other. We have increased the system size 25 times and observed no fundamental changes rather than seeing a multiple copy of what we have observed (see movie S12). It is obvious that the radius ratio, interaction mode, and strength of the small colloids can help to control the bond angle of the small colloids in the colloidal molecules. These results provide a possible way to manipulate the configuration and bond angle of colloidal molecules by adjusting their size ratio and surface parameters.

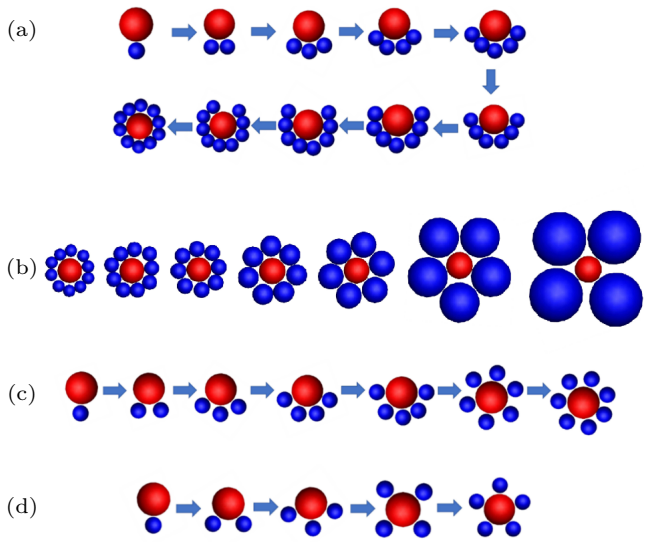


Fig. 6. Self-assembly of active colloidal molecules with coordination numbers and bond angles controlled by the surface activity of the small colloid. For (a) the radius ratio is 0.5 and the surface parameters are $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = 0.0$, $\tilde{\mu}_B = -1.0$; for (b) the radius ratios are 0.5, 0.6, 0.65, 0.85, 1.0, 1.5, 2.0 from left to right and the surface parameters are $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = 0.0$, $\tilde{\mu}_B = -1.0$; for (c) the radius ratio is 0.5 and the surface parameters are $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = -0.5$, $\tilde{\mu}_B = -1.0$; for (d) the radius ratio is 0.5 and the surface parameters are $\tilde{\alpha}_A = 1.0$, $\tilde{\mu}_A = 0.0$, $\tilde{\alpha}_B = -1.0$, $\tilde{\mu}_B = -1.0$.

4. Conclusion and perspectives

Using Brownian dynamics simulations of model active colloidal particles, we have elucidated a variety of dynamical structures induced by diffusiopheresis interaction of active colloids. To capture the basic features of the self-assembled colloidal molecules, only the far-field approximation of the diffusiophoresis interaction is considered, which decays as $1/r$. From our simulation, colloidal molecules of three different dynamic functions are realized, including translation, rotation, and rest. Moreover, we show that colloidal particles with the same surface parameters can form dynamical structures with dynamic functions via breaking their size symmetry. The product of surface activity and surface mobility ($\alpha\mu$) is a key factor which affects the propelling velocity of the active colloidal molecules.

For colloidal particles with equal radius, active colloidal molecules can be formed with different surface parameters, including translational, rotational, and stationary molecules. For some configurations, i.e., AB molecule, they can either be stationary or translational depending on their specific surface parameters, which provides a possible way to control the mobility of colloidal molecules by altering their surface parameters.

Colloidal particles with different radii can break the symmetry of geometry, forming some self-propelled molecules and resting colloidal molecules. Typically, AB_n are formed with monodispersed colloids. Altering the surface parameters of the small colloids can easily change the bond angle. Specifically, in the current study, increasing the repulsion among the small colloids will increase the bond angle.

The current model captures the basic self-assembly and active behavior of active colloidal molecules in a small domain and a small number of particles quite well. More simulations, with even more colloidal particles and perhaps more species of surface parameters, may be required to explore whether the current diffusionpheresis model can be extended to study and predict more complex situation of colloidal particles. In this area, computationally efficient models and schemes such as the one we adopted in the current paper may provide a prag-

matic tool and some qualitative results for real active colloids systems.

Acknowledgment

We would like to thank Professor Scott A. Edwards from Shenzhen University for stimulating discussion.

References

[1] Blaaderen A V 2003 *Science* **301** 470
[2] Poon W 2004 *Science* **304** 830
[3] Löwen H 2018 *Europhys. Lett.* **121** 58001
[4] Gao Y, Mou F, Feng Y, Che S, Li W, Xu L and Guan J 2017 *ACS Appl. Mater. Interf.* **9** 22704
[5] Sánchez S, Soler L and Katuri J 2015 *Angew. Chem., Int. Ed.* **54** 1414
[6] Wang W, Duan W, Ahmed S, Mallouk T E and Sen A 2013 *Nano Today* **8** 531
[7] Malins A, Williams S R, Eggers J, Tanaka H and Royall C P 2009 *J. Phys.: Condens. Matter* **21** 425103
[8] Palagi S and Fischer P 2018 *Nature Reviews Materials* **3** 113
[9] Ozin G A, Manners I, Fournier-Bidoz S and Arsenault A 2005 *Adv. Mater.* **17** 3011
[10] Marchetti M C, Joanny J F, Ramaswamy S, Liverpool T B, Prost J, Rao M and Simha R A 2012 *Rev. Mod. Phys.* **85** 1143
[11] Timm U and Okubo A 1995 *Bull. Math. Biol.* **57** 631
[12] Ballerini M, Cabibbo N, Candelier R, Cavagna A, Cisbani E, Giardina I, Orlandi A, Parisi G, Procaccini A, Viale M and Zdravkovic V 2008 *Anim. Behav.* **76** 201
[13] Moussaid M, Garnier S, Theraulaz G and Helbing D 2009 *Top. Cogn. Sci.* **1** 469
[14] Rouet P E, Chomette C, Duguet E and Ravaine S 2018 *Angew. Chem., Int. Ed.* **57** 15754
[15] Duguet E, Désert A, Perro A and Ravaine S 2011 *Chem. Soc. Rev.* **40** 941
[16] Anderson J L 1989 *Ann. Rev. Fluid Mech.* **21** 61
[17] Abecassis B, Cottin-Bizonne C, Ybert C, Ajdari A and Bocquet L 2008 *Nat. Mater.* **7** 785
[18] Moran J L and Posner J D 2017 *Annu. Rev. Fluid Mech.* **49** 511
[19] Soto R and Golestanian R 2014 *Phys. Rev. Lett.* **112** 068301
[20] Golestanian R, Liverpool T B and Ajdari A 2007 *New J. Phys.* **9** 126
[21] Popescu M N, Tasinkevych M and Dietrich S 2011 *Europhys. Lett.* **95** 28004
[22] Sabass B and Seifert U 2010 *Phys. Rev. Lett.* **105** 218103
[23] Michelin S, Lauga E and Bartolo D 2013 *Phys. Fluids* **25** 061701
[24] Howse J R, Jones R A, Ryan A J, Gough T, Vafabakhsh R and Golestanian R 2007 *Phys. Rev. Lett.* **99** 048102
[25] Hong Y, Diaz M, Córdova-Figueroa U M and Sen A 2010 *Adv. Funct. Mater.* **20** 1568
[26] Gao W, Feng X, Pei A, Gu Y, Li J and Wang J 2013 *Nanoscale* **5** 4696
[27] Pavlick R A, Sengupta S, McFadden T, Zhang H and Sen A 2011 *Angew. Chem., Int. Ed.* **50** 9374
[28] Rapaport D C 2004 *The Art of Molecular Dynamics Simulation*, 2nd edn. (Cambridge: Cambridge University Press) p. 15
[29] Frenkel D and Smit B 1996 *Understanding molecular simulation: from algorithms to applications*, 2nd edn (Boston: Academic Press) p. 48