

# Electronic Supplementary Information for “Active colloid with externally induced periodic bipolar motility and its cooperative motion”

Airi N. Kato, Kazumasa A. Takeuchi, and Masaki Sano

## Supplementary Note 1: Model of a single self-propelled particle with a sinusoidal and constant velocity

Consider a particle self-propelling at speed  $v(t)$  under the effect of translational and rotational diffusion. The translational diffusion and rotational diffusion coefficients are denoted by  $D$  and  $D_\theta$ , respectively. Let  $\mathbf{x}$  and  $\theta$  be the position and the propelling direction, respectively. The equations of motion read:

$$\dot{\mathbf{x}}(t) = v(t)\hat{\mathbf{n}}(t) + \boldsymbol{\zeta}(t) \quad (\text{S1})$$

$$\dot{\theta}(t) = \xi(t). \quad (\text{S2})$$

Here,  $\hat{\mathbf{n}}(t) = (\cos \theta(t), \sin \theta(t))$  is the propelling direction vector. The noises are white Gaussian:  $\langle \zeta_i(t)\zeta_j(t') \rangle = 4D\delta(t-t')\delta_{ij}$ ,  $\langle \zeta_i(t) \rangle = 0$ ,  $\langle \xi(t)\xi(t') \rangle = 2D_\theta\delta(t-t')$ , and  $\langle \xi(t) \rangle = 0$  for arbitrary  $t, t'$ . Here let us assume the self-propulsion velocity  $v(t)$  to be

$$v(t) = v_0 + v_1 \cos \omega t. \quad (\text{S3})$$

We calculate the energy power spectrum of this model via the velocity autocorrelation. The velocity autocorrelation is calculated as follows.

$$\begin{aligned} \langle \mathbf{v}(t_1) \cdot \mathbf{v}(t_2) \rangle &= v(t_1)v(t_2)\langle \hat{\mathbf{n}}(t_1) \cdot \hat{\mathbf{n}}(t_2) \rangle + 4D\delta(t_1 - t_2) \\ &= v(t_1)v(t_2)\langle \cos \theta(t_1) \cos \theta(t_2) + \sin \theta(t_1) \sin \theta(t_2) \rangle + 4D\delta(t_1 - t_2) \\ &= v(t_1)v(t_2)\langle \cos(\theta(t_1) - \theta(t_2)) \rangle + 4D\delta(t_1 - t_2) \\ &= v(t_1)v(t_2)\langle \cos(\Delta_{t_1-t_2}\theta) \rangle + 4D\delta(t_1 - t_2), \end{aligned} \quad (\text{S4})$$

where  $\Delta_\tau\theta := \theta(t + \tau) - \theta(t)$  and the time translation invariance of  $\theta(t)$  is taken into account. The probability density of  $\Delta_\tau\theta$ , denoted by  $P(\Delta\theta, \tau)$ , has the characteristic function that satisfies  $\phi(s, t) := \int_{-\infty}^{\infty} d\theta P(\theta, t)e^{i\theta s} = e^{-D_\theta s^2 t}$ . For  $\tau > 0$ ,

$$\begin{aligned} \langle \cos(\Delta_\tau\theta) \rangle &= \int P(\theta, \tau) \cos \theta d\theta \\ &= \frac{\phi(1, \tau) + \phi(-1, \tau)}{2} \\ &= e^{-D_\theta \tau}. \end{aligned} \quad (\text{S5})$$

Therefore, neglecting the translation diffusion, we obtain the following expression for the velocity autocorrelation:

$$\begin{aligned} \langle \mathbf{v}(t_1) \cdot \mathbf{v}(t_2) \rangle &= v(t_1)v(t_2)e^{-D_\theta|t_1-t_2|} \\ &= [v_0^2 + v_0v_1 \{\cos(\omega t_1) + \cos(\omega t_2)\} + v_1^2 \cos(\omega t_1) \cos(\omega t_2)] e^{-D_\theta|t_1-t_2|} \end{aligned} \quad (\text{S6})$$

which cannot be expressed as a function of  $(t_1 - t_2)$ . In other words,  $\langle \mathbf{v}(t_1) \cdot \mathbf{v}(t_2) \rangle$  is not invariant under time translation.

Generally, the energy spectral density is calculated by the Fourier transformation of the velocity autocorrelation  $\langle \mathbf{v}(t) \cdot \mathbf{v}(t + \tau) \rangle$ . In our model, however,  $\langle \mathbf{v}(t) \cdot \mathbf{v}(t + \tau) \rangle$  cannot be expressed by a function of  $\tau$  only. Therefore, here we consider the periodically-averaged velocity correlation  $C(\tau) := \overline{\langle \mathbf{v}(t) \cdot \mathbf{v}(t + \tau) \rangle}$ , where the overline denotes averaging over a period of the external field. This is evaluated as follows:

$$\begin{aligned} C(\tau) &= \left( v_0^2 + v_1^2 \overline{\cos(\omega t) \cos(\omega(t + \tau))} \right) e^{-D_\theta \tau} \\ &= \left( v_0^2 + \frac{v_1^2}{2} \overline{(\cos(2\omega t + \omega\tau) + \cos(\omega\tau))} \right) e^{-D_\theta \tau} \\ &= \left( v_0^2 + \frac{v_1^2}{2} \cos(\omega\tau) \right) e^{-D_\theta \tau}. \end{aligned} \quad (\text{S7})$$

Then, the spectral density  $S(f)$  is obtained by Fourier transform of Eq. (S7), as follows:

$$S(f) = v_0^2 \frac{2D_\theta}{D_\theta^2 + (2\pi f)^2} + \frac{v_1^2}{2} \left( \frac{D_\theta}{D_\theta^2 + (\omega + 2\pi f)^2} + \frac{D_\theta}{D_\theta^2 + (\omega - 2\pi f)^2} \right), \quad (\text{S8})$$

when the translational diffusion is neglected. The translational diffusion adds a constant terms to Eq. (S8). For low frequency  $f$ , the first term is dominant in Eq. (S8), which is Lorentzian with the cutoff frequency  $f \sim \frac{D_\theta}{2\pi}$ .

To estimate  $D_\theta$ , we consider the experimentally observed low-frequency region to be a simple Lorentzian: the first term of Eq. (S8)  $v_0^2 \frac{2D_\theta}{D_\theta^2 + (2\pi f)^2} = \frac{2v_0^2}{D_\theta} \cdot \frac{1}{1 + (2\pi f/D_\theta)^2}$ . The coefficient  $\frac{2v_0^2}{D_\theta}$  was determined by the value at  $f = 0$ . By fitting the data for  $f < 40$  Hz, we obtained  $D_\theta \sim 31.4 \pm 0.6 \text{ s}^{-1}$  ( $D_\theta^{-1} \sim 0.03 \text{ s}$ ). Note that this effective rotational diffusive coefficient  $D_\theta$  is athermal, can be originated from such as surface heterogeneity of the electrode and particles. (Cf. thermal rotational diffusive coefficient:  $D_\theta^{\text{thermal}} = \frac{k_B T}{8\pi a^3 \eta} \sim 10^{-3} \text{ s}^{-1}$  with the room temperature  $T$  and the viscosity of hexadecane  $\eta$ .)

## Supplementary figures

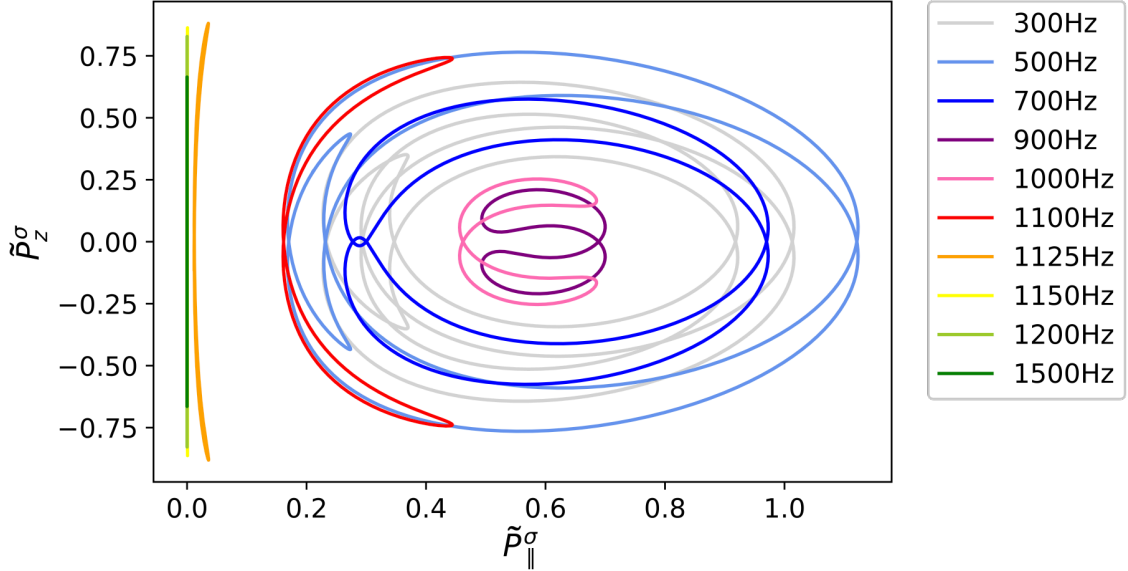


Figure S1: Periodic states of the single-particle model for different frequencies of the external electric field. Trajectories from initial conditions with  $\tilde{P}_\parallel^\sigma(0) > 0$  are shown, in  $(\tilde{P}_\parallel^\sigma, \tilde{P}_z^\sigma)$  space. For high enough frequencies,  $\tilde{P}_\parallel^\sigma$  vanishes and the particle does not reciprocate (see Eq.(10) in the main paper).

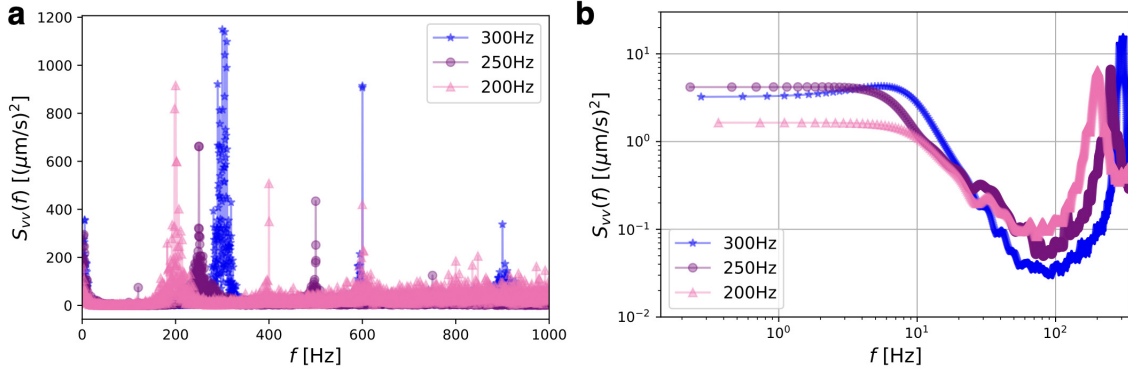


Figure S2: Experimental results of the energy spectral density of particles forming a doublet, for different frequencies of the external electric field. The amplitude was kept at 150 V (root-mean-square amplitude). The motion of the particles was captured at the frame rate 10 times faster than the external frequency (e.g., 2500 fps for 250 Hz). The highest peak of each spectrum is found at the frequency of the external field, corresponding to the reciprocating motion of the particles. The second harmonic peak due to the dipole-dipole interaction is also seen in all cases. Panel (b) shows an enlargement of (a) in a low-frequency region. To reduce statistical fluctuations, the time series were divided into 30 segments (each segment contains 36 periods), then the power spectra were averaged. All spectra show a similar low-frequency mode.

## Supplementary Note 2: Possible effects of surface roughness of ITO electrode and its interaction with particle surface

To discuss the possibility that the athermal value of the rotational diffusion coefficient results from surface heterogeneity of the electrode, we measured the surface roughness of the indium-tin oxide (ITO) film on the glass substrate used in the experiments (Mitsuru Optical Co. Ltd.) with an atomic force microscope (AFM, Bruker, Dimension FastScan Bio). The standard deviation of the height fluctuations is 3.8 nm (Fig. S3a). Histogram of the height fluctuations is close to a Gaussian distribution and the power spectrum of the height fluctuations is close to a Lorentzian. From the fitting, we obtained the characteristic wavelength to be  $\lambda \sim 0.75 \mu\text{m}$ . External mechanical perturbations to the moving particle on a rough substrate can be estimated from potential energy calculations. The potential energy fluctuations calculated by assuming that the particle is moving along the ITO surface landscape are less or of the same order of the thermal fluctuation  $k_B T$ . However, surface roughness of the order of 4 nm is close to the size of Debye length of the surface double layer of the particle. This Debye length level of roughness may cause even stronger fluctuations in the flow of charge around the particle and its distribution, which may have a significant impact on the effective rotational diffusion of the particle. Since the mean speed of the particles averaged over the period of the externally applied electric field is about  $v_m \sim 60 \mu\text{m/s}$  and the characteristic time of the Lorentzian in Fig.3b is  $\tau \sim 0.032$  s, the number of fluctuation events experienced by a particle within  $\tau$  is estimated by  $n \sim v_m \tau / \lambda$ . We obtained  $n \sim 2.4$ . This number of fluctuation events is sufficient to cause loss of orientation information and result in athermal rotational diffusion of the particle.

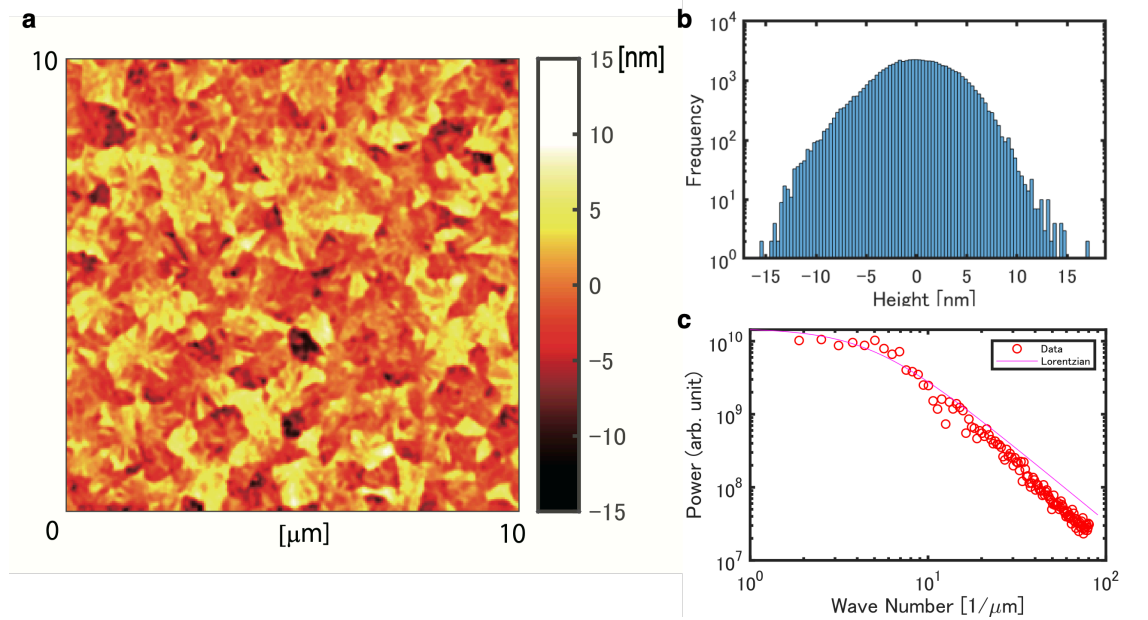


Figure S3: Measurement of surface roughness of ITO substrate. (a) Height roughness of the ITO coat on the glass substrate measured with an AFM ( $xy$ -area size:  $10 \times 10 \mu\text{m}^2$ ).  $Z$ -range of color-coded image is 32.7 nm. (b) Histogram of height fluctuations. Standard deviation of the height fluctuation is 3.8 nm. (c) Radial distribution of the height fluctuation power spectrum in  $k$ -space calculated from the two-dimensional Fourier transformation of the height fluctuations. Lorentzian fit gives a characteristic wavenumber of  $4.8 \mu\text{m}^{-1}$ . (wavelength  $\sim 0.75 \mu\text{m}$ )

## Supplementary videos

- **Video S1 (S1.mov): Short-time behavior of an isolated particle.** The particle reciprocates at the external frequency (300 Hz), though it is only barely visible in the movie. The movie is played at 0.01 times the real speed.
- **Video S2 (S2.mov): Long-time behavior of an isolated particle (stroboscopic).** This movie shows long-time persistent motion of the particle. The frame acquisition rate is set to be equal to the external frequency (300 Hz). The movie is played at 0.1 times the real speed.
- **Video S3 (S3.mov): A wide-field video (x10 objective) showing multiple clusters (stroboscopic, 250 Hz).** Clusters are formed and maintained longer than 1000 periods if they do not encounter other particles. The movie is played at 0.1 times the real speed.
- **Video S4 (S4.mov): Short-time behavior of a doublet (300 Hz).** The two particles reciprocate at the external frequency in a cooperative manner. The propelling directions tend to align, but not always. The movie is played at 0.01 times the real speed.
- **Video S5 (S5.mov): Long-time behavior of a doublet (stroboscopic, 300 Hz).** The two particles show persistent motions, with the interparticle distance fluctuating but kept in some range. The movie is played at 0.1 times the real speed.
- **Video S6 (S6.mov): Short-time behavior of a doublet (250 Hz).** The two particles reciprocate at the external frequency in a cooperative manner. The propelling directions tend to align, but not always. The movie is played at 0.01 times the real speed.
- **Video S7 (S7.mov): Long-time behavior of a doublet (stroboscopic, 250 Hz).** The two particles show persistent motions, with the interparticle distance fluctuating but kept in some range. The movie is played at 0.1 times the real speed.

- **Video S8 (S8.mov): Short-time behavior of a triplet (300 Hz).** The three particles reciprocate at the external frequency (300 Hz) in a cooperative manner. The propelling directions tend to align, but not always. The movie is played at 0.01 times the real speed.
- **Video S9 (S9.mov): Long-time behavior of a triplet (stroboscopic, 300 Hz).** The three particles show persistent motions, with the interparticle distances fluctuating but kept in some range. The movie is played at 0.1 times the real speed.
- **Video S10 (S10.mov): Short-time behavior of a triplet (250 Hz).** The three particles reciprocate at the external frequency in a cooperative manner. The propelling directions tend to align, but not always. The movie is played at 0.01 times the real speed.
- **Video S11 (S11.mov): Long-time behavior of a triplet (stroboscopic, 250 Hz).** The three particles show persistent motions, with the interparticle distances fluctuating but kept in some range. The movie is played at 0.1 times the real speed.
- **Video S12 (S12.mov): Long-time behavior of a triplet formation (stroboscopic, 300 Hz).** An initially isolated particle joined a doublet and formed a triplet. The shape of the triangle formed by the three particles dynamically changes. The movie is played at 0.1 times the real speed.