Motion-Reversal in Colloidal Walkers

by

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Abstract

In this research, the manipulation of colloidal systems composed of superparamagnetic particles in water is studied by a simulation method. In response to an external magnetic field, the dipoles drive the beads to self-assemble into chains, which rotate and consequently move across a nearby surface. Under strong surface-interaction, the dynamic and equilibrium structures are modeled using a Bell model and measured using Monte Carlo-type update steps. It is shown that the walking motion can be characterized as two different regimes corresponding to an increase of the rotating arm from half to all of the chainlength as the activation barrier of binding interaction increases with a constant overall increase in energy. When operating at rotational frequencies from 1 Hz to 9 Hz and applied field from 1 mT to 9 mT, the corresponding translational velocities of chain-like rotors can be approximated with a two-state model until the fragmentation transition of chain-like rotors takes place. The translational velocities of chain-like rotors scale linearly with respect to number of beads.
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Introduction

Biological flows in response to environmental signals is important for survival of creatures. In order to design functional assemblies that allow transport in organism\(^4\) based on relevant principles, some examples of transporting systems in nature such as flagella, cilia, and chemotaxis are widely studied theoretically and experimentally.\(^{[1][2][3][4]}\) Active microscopic robots are especially considered as one of the possibilities allowing control of flows at fine level, which make advances in microfluidics and sensing approachable. In order to use these rotor systems to controllably manipulate surface flows on the microscale on a specific walking surface, such as a surface coated with ligand-receptor pairs, the understanding of relevant physical properties is important. For this purpose, simulation study of manipulating colloidal systems of several superparamagnetic particles in a liquid is conducted to design chemotactic microscopic robots. By turning off and on the magnetic field, the disassembly and reassembly of the superparamagnetic beads can be dynamically controlled. When the rotating magnetic field is imposed, several particles are attracted by each other and assembled as a rotor with chain-like configurations by the induced magnetic moments.\(^{[5][6]}\) In this system of interest, a no-slip boundary condition increases friction near the surface and enables the translational motion of line-up beads to be dynamically controlled by an external magnetic field. Previous work has experimentally and theoretically studied the velocity of the surface walker under an applied rotational magnetic field in detail. As a continuation of previous study, this study is aimed to research the dynamic behaviors under strong frictional force on surface.

In this study, a coarse-grained Brownian dynamic model is used to demonstrate the dynamic behaviors of a superparamagnetic rotor as a response to the roughness of the surface. The roughness of the surface is effectively modeled kinetically by the binding and
unbinding characteristics of bead systems to the surface, using a Monte-Carlo-type update step that describes the reactions using the Bell Model. Meanwhile, hydrodynamic theories are subsequently applied to model the motion of rotors in the broader context of diffusion-related motion properties.
METHOD

Brownian dynamics

Brownian dynamics model is used to develop the dynamics of superparamagnetic cores with no dominations of acceleration. If we assume that the response to the system under small perturbation is linear, the response to an applied force can be considered the same as response to a spontaneous fluctuation.

\[ D_{ij} = \mu_{ij}k_BT \]  

where \( \mu_{ij} \) is the mobility matrix for hydrodynamic interactions between beads based on Blake's tensor under restriction of finite bead size to first order.\[8\] The \( D_{ij} \) is the diffusion tensor. The force exerted on the beads is given by the summation of repulsive inter-force between beads, boundary repulsive force between beads and wall, magnetic dipole-dipole force, gravitational force, and binding forces. Here, we assume the magnetic field is large enough compared to noise from thermal interaction.

Fig. 1: The schematic plot of a walking rotor composed of four beads considered in this study.

Environment and Initial Configuration

The superparamagnetic beads are simulated using coarse grain model for colloidal particles with a radius R of \( \mu \)m and a susceptibility of 1.4. We assume that the sizes of interested particles are significantly larger than molecules in the liquid, but are still within the regime that resulting collisions with water molecules are effective enough for Brownian
motion. The initial configuration of the rotor starts with a position parallel to both the interaction surface and rotation surface of a magnetic field. (Fig. 1) The distance between every two beads is initially set to 2.5 $R$. As a variable to control the frictional force, the reaction distance from the surface is 1.3 $R$ for all simulation time. As time progresses, the magnetic moment on the beads are then updated every time step by given magnetic field strength and rotation frequency, which are 1-9 mT and 1-10 Hz in this study, respectively.

**Magnetic Interaction**

The magnetic moment $m$ of beads in the linear response regime is

$$m = \frac{V\Delta\chi}{\mu_0}B$$

(2)

where $B$ is the magnetic field, $\mu_0$ is the permeability of free space, $V$ is the volume of the bead, and $\Delta\chi$ is the effective susceptibility.

In our study, we consider the interaction between every two beads at position $r_i$ and $r_j$ with a difference $r = r_i - r_j$, and $r = |r|$. Here, we consider the overall effective magnetic force $F = F_e + F_m$ composed of external $F_e$ and inducted field $F_m$ between dipoles. Based on magnetic field strength at a point from a dipole

$$B = \frac{\mu_0}{4\pi r^3} \left[ 3 \left( \frac{m \cdot r}{r^3} \right) r - m \right]$$

(3)

The gradients give the dipole-dipole force acting on a dipole at $r_i$ from a dipole at $r_j$:

$$F_{dd} = \frac{F_0 R^4}{r^4} \left[ \left( \frac{\mathbf{m}_i \cdot r}{r} \right) \mathbf{m}_j + \left( \frac{\mathbf{m}_j \cdot r}{r} \right) \mathbf{m}_i - \left( \frac{5}{r^2} \left( \frac{\mathbf{m}_i \cdot r}{r} \right) \left( \frac{\mathbf{m}_j \cdot r}{r} \right) - \mathbf{m}_i \cdot \mathbf{m}_j \right) \frac{r}{r^3} \right]$$

(4)

with $F_0 = \frac{4\pi}{3\mu_0} (Rf\Delta\chi B_0)^2$. Based on experimental data, $F_0 \sim 100 \frac{kT}{R}$ is used.
Inter-particle steric interaction

In order to model the volume exclusion property, we assume the excluded volume potential is infinitely large. A modified Lennard-Jones potential between beads is applied for computational convenience

\[ F_{LJ}(r) = \frac{\varepsilon}{r - 2R} \left( \frac{\sigma}{r - 2R} \right)^{12} - \left( \frac{\sigma}{r - 2R} \right)^{6} \approx \frac{\varepsilon}{r - 2R} \left[ - \left( \frac{\sigma}{r - 2R} \right)^{6} \right] \tag{5} \]

where \( \varepsilon \) is the depth of potential, \( \sigma \) is where the zero point of steric force locates, \( r \) is the distance between centers of beads, and \( R \) is the radius of the bead. We utilize \( \varepsilon = 0.1R \), and \( \varepsilon = 0.02 \ kT/R \). The attracting term is neglected.

Particle-surface repulsive interaction

In order to simulate the non-overlapping behavior between particle and surface, a similar force exerts by wall to the beads reads

\[ F_z(r) = \frac{\varepsilon}{r_z - 2R} \left( \frac{\sigma}{r_z - 2R} \right)^{12} - \left( \frac{\sigma}{r_z - 2R} \right)^{6} \approx \frac{\varepsilon}{r_z - 2R} \left[ - \left( \frac{\sigma}{r_z - 2R} \right)^{6} \right] \tag{6} \]

where \( r_z \) is the distance from the surface to the center of the bead.

Gravitational force

The beads are assumed to be located at the Earth's surface with effective gravitational acceleration \( F_g = -\Delta \rho Vg \), with \( g = 9.8 \ \text{m/s}^2 \), the difference between the bead and liquid (water)

\[ \Delta \rho = 0.8 \ \text{g/cm}^3, \] and the bead volume as a sphere \( V = \frac{4\pi R^3}{3} \).

Particle-surface binding interaction

In order to study the dynamics of beads under strong binding interaction to surface, harmonic springs are added to beads for mobility restriction. Once bound to the surface, a z-
direction attractive force are added to beads within the reaction radius $= 1.3 \, r$ with respect to surface. Also, the beads are restricted in directions parallel to surface by two harmonic springs. The three spring constants are chosen to be $200 \, \frac{kT}{R^3}$.

**Equilibrium structure**

![Energy landscape](image)

Fig. 2: The energy landscape of binding-unbinding transition for surface walkers.

The interaction between the beads within reaction radius with respect to the surface and the surface is modeled by an energy landscape shown in Fig. 2. The activation energies of bound EB and unbound EUB states define the reaction energy $\Delta E$ and thus the equilibrium structure of systems. Initially unbound, the state of each bead locates within the reaction radius is bound randomly with a probability controlled by activation barrier EB, while the activation energy EUB controls the probability of transition from bound state to unbound state.

\[
P_B = e^{-\frac{EB}{k_B T}} \tag{7}
\]

\[
P_{UB} = e^{-\frac{EUB}{k_B T}} \tag{8}
\]
where $k_B$ is Boltzmann's constant, $E_B$ is the activation barrier to bind, and $E_{UB}$ is the activation barrier to unbind once the bead is bound. The binding process is simulated with the Monte Carlo method. Initially, all the beads are in the unbound state. With a resolution of every ten time steps, each bead locates within a reaction-radius-cutoff is randomly assigned with a normalized number. A transition in the state, either from the bound state to the unbound state or from the unbound state to the bound state, takes place when the normalized number is higher than the probability of state transition shown in equation 7, while the probability of state transition is corrected to first order in a stepwise fashion. This enables us to study the dynamics of rotor system under strong interaction to surface.

In order to simulate the behavior that the beads within reaction radius experiencing larger dragging force when approaching the surface, a spring force is added to modified the backward activation barrier once a bead is bound. This results in a distortion in original energy landscape shown in Fig. 3.

$$E_{UB}' = E_{UB} - \langle f \rangle \Delta z$$

Fig. 3: The modified energy landscape of binding-unbinding transition for beads of surface walkers once bound.
where $k$ is the spring constant of the dragging force, and $\Delta k$ is the depth the bead stay within the reaction radius.

**Parameters**

Here, we devise the characteristic timescale as fundamental unit of simulation based on Einstein Relation. In this study, we thus use a rotational frequency between 1 Hz to 9 Hz, and an applied magnetic field within 1 mT to 9 mT based on experiments.[5] Assuming that the response is faster than the characteristic timescale of particles motion, we simulate the motion by solving dynamic equations at each time step with a given initial condition. For each experiment, a time step of $5 \times 10^{-4}$ in units of characteristic timescale is simulated for $3 \times 10^7$ iterations. The product leads to the total period of simulated time $1.5 \times 10^4 \tau$. This corresponds to at least 15 full rotations for results of the translational velocity.
Two states can be defined to describe the walking behaviors of rotors as a function of overall change in energy under a constant forward activation barrier to simulate a frictional surface. When walking on a surface with a large overall change in energy for the binding process, the rotors move with a relatively low translational velocity (Fig. 4). The corresponding velocity results converge to the ones shown in a previous study that, with this large overall change energy limit, the translational velocity is primarily driven by the hydrodynamic forces instead of the surface-binding force acting on rotors.[5] As the backward activation barrier and the overall change in energy increase under a constant forward activation barrier, the probability for beads in bound state to unbind decreases exponentially. The beads are then more likely to remain in a bound state. This leads to a locally hindering effect of mobility on beads near the surface. As the lower beads (the ones closest to the surface) bind to the surface without experiencing the fragmentation transition (the rotor breaks into fragments composed of several beads instead of a whole single chain of beads), it is observed that the chain-like rotor undergoes a rotating motion with a rotating angle around the bound lower bead as a pivot (Fig. 5). As the backward activation barrier and thus the duration time in which the endmost bead remains in a bound state increase, this rotating behavior as a result from the surface-binding leads to a significant increase in the translational velocity of rotor walking along the surface.
Fig. 4: The calculated and simulated translational velocity of the C.O.M of the rotor with four beads increases with $\Delta E$, and then drops due to chain breakup. The rotational frequencies are set at 1, 3, 5, and 7 Hz. The forward activation barrier is 6 kT.

Fig. 5: The rotors walking on surface with a 6 kT forward activation barrier under 1 Hz rotating magnetic field at 9 mT. The backward activation barriers are 1.5 kT and 8 kT, respectively.

A rotational angle can be defined to characterize two states. As a measure of the difference of angles at which the rotor attaches to and detaches from the surface, the rotational angle approaches 0° in the high $\Delta E$ regime and increases to an angle up to 180° depending on the rotating frequency and the applied field as $\Delta E$ decreases (Fig. 6). This corresponds to a shift in the position of the rotating center from C.O.M of the rotor to the endmost bead. The “arm”
of the rotation is thus doubled from half of the chain-length to the overall length.

![Image: The defined rotational angle.](image)

To characterize the system using the two-state model mentioned above, we introduce a quantity $\tau_b$, which tracks the number of time steps that at least one bead remains in bound state over total accessible simulation time. Assume that the translational velocity of a rotor when remaining in the two dynamic states is linearly scalable, the translational velocity of a rotor under a full rotation of the magnetic field could be approximated as a function of $\tau_b$

$$V_{\text{cal}} = \tau_b \times 4(N - 1) + (1 - \tau_b) \times V_{\text{hydro}}$$

where the $V_{\text{hydro}}$ is the converged translational velocity of a rotor on a surface with a high $\Delta E$ limit. The translational velocity curve under either a very high or low $\Delta E$ regime matches with the calculated velocity due to the dominating behavior of one of the two dynamic states (Fig. 7). In a low $\Delta E$ regime, the simulated velocity closely follows our calculated one until the rotor enters the fragmentation transition, which often leads to an immediate chain breakup and a drop in velocity. When operating with a high rotational frequency, a rotor starts breaking in relatively higher $\Delta E$ regime due to the large difference between the characteristic binding time-scale and the rotating time-scale.
This translational velocity $V_{cai}$ of the system derived by the two-state model is also universally scalable for rotors walking on a same frictional surface with different chain-lengths, where the calculated velocity $V_{cai}$ is given by equation 1. (Fig. 8) However, it was observed in the simulation that several factors result in non-linear behaviors between the number of beads and the velocity as rotors composed of more beads are used to simulate. As the number of beads increases from two, it is statistically rare for all the bound beads to detach simultaneously from surface. Also, a rotor composed of more beads is more likely to go into fragmentation transition. In addition, the large difference in the characteristic time-scale of binding behavior and the rotation leads to a bending instead of chain-like configuration of rotors. This results in the reduction of effective rotating arm for pivoting motion especially under low overall-change-in-total-energy limit. Accordingly, the simulation result $V_{sim}$ of rotor with higher number of chain-length is expected to be lower than predicted velocity $V_{sim}$. Besides, the frequent fragmentation and reassembled behavior of rotor at low overall change in total energy limit also results in a reduction in the effective
Fig. 8: The translational velocity of 4-bead rotor with respect to the number of beads under an applied field of 9 mT, a forward activation barrier of 6 kT, and a rotational frequency of 1 Hz.

\[ V_{\text{sim}} = b + \frac{a_{\text{fit}} e^{-\Delta E}}{1 + e^{-\Delta E}} \]  

To further characterize the system, the translational velocity of rotors is fitted with respect to the overall change in total energy based on the two-state model. The constant \(a_{\text{fit}}\) derived from the fitted equation closely agrees with the calculated difference between velocities of two dynamic states

\[ a_{\text{cal}} = 4 \times (N - 1) - V_{\text{hydro}} \]  

The relation between parameter \(a_{\text{cal}}\) and number of beads \(N\) is analyzed. According to the analytic form of velocity driven by hydrodynamic force derived in the previous study, the velocity scales linearly with number of beads. [5] As a result, the difference of velocity between two dynamic states \(a_{\text{cal}} \sim a_{\text{fit}}\) also scales linearly with respect to the number of beads of the rotor, which is shown in Fig. 8.
The dependence of the parameter $a_{fit}$ on the rotational frequency is also discussed. (Fig. 9) Under low rotational frequency, the fitted parameter $a_{fit}$ closely follows the calculated parameter $a_{cal}$ due to two reasons: First, the large difference in the characteristic time-scale between the binding event and the rotating event, which results from low rotational frequency of magnetic field, prevents the rotor from breaking up during a pivoting motion. Second, a low rotational frequency compared to characteristic binding frequency keeps rotors in a chainlike configuration instead of a bent geometry when attaching at or detaching from the surface. Since the calculated parameter $a_{cal}$ is introduced based on the assumption that neighboring beads of rotor are all equally spaced, the corresponding model is more appropriate for the velocity of a chainlike rotor.
Fragmentation

The fragmentation of rotors may take place as the magnetic torque, the hydrodynamic torque, the torque contributed by gravity, and the frictional torque balance in magnitude. As the lower beads of a rotor are in a bound state, a large difference between the time-scale corresponding to the rotation of the applied field and the binding time-scale leads to a chain breakup. This fragmentation is particularly significant as rotors walk on a surface with strong surface interaction with a large rotational angle, which pushes beads closer to the surface where they experience stronger frictional force. As more beads locate within the reaction regime and remain in bound state in the same time step, it is statistically less likely for them to unbind simultaneously. This prevents a rotor from walking forward continuously and leads to fragmentation close to the surface.

Different forward activation barrier EB

Fig. 10: The translational velocity of rotor under different activation barriers $EB$ and total change of energy $\Delta E$. The frequency of rotating field is 1 Hz, and the applied field is 9 mT.

The activation barrier $EB$ and total change of energy $\Delta E$ were altered to study a rotor system walking on surfaces with a low distribution of binders. (Fig. 10) It was observed in
the simulation that a certain threshold of the activation barrier $EB$ is required for rotors to sustain a positive velocity in the forward direction. Under a low total change of energy $\Delta E$, raising the forward activation barrier $EB$ increases the translational velocity until binding events are statistically rare to take place. As the activation barrier $EB$ increases, the rotor may enter its fragmentation state as the magnetic torque, the hydrodynamic torque, torque contributed by gravity, and torque from binding exerted on the rotor balance in magnitude.

**Backward rotors**

It was also observed that as the backward activation barrier and thus $\Delta E$ gradually increase, the rotor first moves backward and then forward in the translational direction by rotating. This backward behavior, which cannot be quantified by our simple model, was observed at the transit state between the two states described above and is especially significant under strong frictional force. As a rotor attaches to the surface, the center of mass of the rotor is brought closer to the surface and forward in the direction parallel to the surface by the magnetic force. On the other hand, as a rotor detaches from the surface, the center of mass is dragged backward and further from the surface in the normal direction. Due to the strength of the partial force in the normal direction, the angles that the rotor attaches and detached from the surface are not symmetric with respect to normal direction. From the simulation results, the backward behavior of motion and the asymmetry of detaching and attaching angle were observed as the binding event takes place frequently and only lasts for short duration of time.
Velocity-Delta \( E \), 2beads, \( EB = 6 \text{ kT} \), \( B = 9 \text{ mT} \)

Fig. 11: The translational velocity of a 2-bead rotor under an applied field of 9 mT and a forward activation barrier 6 kT.

A backward behavior can be clearly observed in positive \( \Delta E \) regime. (Fig. 11) The difference is especially significant when the rotational frequency of applied field is low. This is because that low frequency results in longer duration time the lower beads can stay within the reaction barrier per rotating cycle. Accordingly, the time steps that slipping motion can take place within is longer, which leads to a larger slipping effect.

Limitations of the model

This simple model approximates the number of binding time steps as zero in the high \( \Delta E \) regime. However, the number of time steps in which at least one bead locates in bound state over total number of time steps for a full magnetic rotation should be given by

\[
p_{\text{non-fric}} = \frac{1}{\pi} \cos^{-1} \left( \frac{r - r_{\text{rxn}}}{r} \right)
\]
as the reaction radius is considered. Assume the translational velocity of rotor when remain in the two dynamic states are linearly scalable, an expression of translational velocity of rotor under a full rotation of magnetic field could be approximated as a function of $\tau_b$

$$V_{cal} = \left[1 - \frac{(1 - \tau_b)}{1 - P_{\text{non-fric}}}\right] \times 4(N - 1) + \frac{(1 - \tau_b)}{1 - P_{\text{non-fric}}} \times V_{\text{hydro}}$$ (13)

However, as the $\Delta E$ decreases, the rotor as a whole is brought closer to the surface by the frictional force, corresponding to changes in rotational angle and center of mass. Accordingly, the variation in the C.O.M position of the rotor in $z$ direction measuring from the surface has to be considered to derive a more accurate translational velocity, which is not included in this study.
Conclusion

By changing the frictional force on the surface, it is demonstrated by simulation study that the translational velocity of a robot composed of superparamagnetic beads driven by a rotating magnetic field in a liquid can be greatly enhanced. As the binding time increases, which is a measure of strength of frictional force on the surface, the center of rotating behaviors of chain-like rotors moves from the center of mass (C.O.M) of the rotor to an endmost bead. This increase in the rotating radius of rotors leads to a significant increase in the translational velocity limited by the total length of the rotor. The enhanced translational velocity in the low $\Delta E$ limit can be approximately by two times of the chain-length per rotating cycle before the rotor goes through the fragmentation transition. This prediction on the translational velocities also applies to rotor-system composed of rotors with different chain-length walking on surfaces with various attaching activation barrier.
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