Hydrodynamic front-like swarming of phoretically active dimeric colloids

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Abstract – Self-propelled phoretic colloids have recently emerged as a promising avenue for the design of artificial microswimmers. Here we show how systems of thermophobic dimeric swimmers can form swarms, in the sense of clusters with an ordered collective net motion. The interplay of attractive hydrodynamic with repulsive phoretic interactions leads to the formation of swarming structures with a flattened geometry in three-dimensional systems. The design of microfluidic devices and of bio-compatible microrobots can benefit from these dynamic and controllable systems.

Introduction. – Synthetic microscale motors are attracting large attention due to their outstanding potential practical applications in fields like microfluidics or microsurgery [1–3]. When the propulsion mechanism is based on phoretic effects [4], such artificial microswimmers have the great advantage of behaving like passive colloids unless they are chemically [1,5,6], electrically [7,8], or thermally activated [9–11]. In particular, thermophoretic swimmers are built from two materials with well differentiated absorption coefficients, like gold and silica, where heterogeneous heating can produce a steady local temperature gradient around the colloid, which translates into its persistent self-propulsion. Thermophoretic swimmers can therefore be powered without any modification of the solvent, what makes them easily bio-compatible. Furthermore, devices engineered with this effect are expected to depict a very large versatility due to two additional facts. One is that thermophoresis has shown to be very sensitive to a large number of factors like pressure, average temperature or solvent composition; and the other is that the heat sources, such as magnets or lasers, can be very precisely controlled in time and space.

Large ensembles of phoretic swimmers are expected to share a large number of properties with other systems of active particles. Chemically active Janus colloidal particles have already shown clustering and self-assembled structures [12–15] as well as schooling behavior; and the formation of living crystals has already been observed for light powered micromotors [16,17]. Brownian simulations of thermophilic active colloids predicted the appearance of clustering and comet-like swarming structures [18,19], and the system dimensionality [20,21] together with the existence and particular form of the hydrodynamic interactions have shown to play a relevant role [22]. Nevertheless, the mechanisms involved in the formation of these structures, the precise importance of the phoretic and hydrodynamic effects, and the behavior of various types of phoretic swimmers are very relevant and still largely unexplored questions. Until now, spherical Janus thermophoretic swimmers have been the only geometry investigated experimentally [9,23,24], although important effects related to particle shape can be expected. Catalytic dimer motors, moving in the direction of the catalytic cap, have already been synthesized [6], which clearly indicates that diffusio- and thermophoretic motion of dimeric colloids in both directions are experimentally feasible.

In this letter, we investigate thermophobic dimer-shaped colloids from the one-particle dynamics to their collective behavior, by means of detailed hydrodynamic simulations in three dimensions. These active colloids constitute a paradigmatic case in which phoretic repulsion and hydrodynamic attraction occur simultaneously. This can result in spontaneous self-assembly of oriented and collectively moving structures, reminiscent of planar order. These remarkable swarming structures appear then to be specific to phoretic active colloids; their direction of motion will be easier to control [25] such that promising applications are to be expected, as those related to...
directed cargo transport [26] or the development of microfluidic devices [27,28].

**Method.** – Simulations are performed with a hybrid mesoscopic approach. Multiparticle collision dynamics (MPC) is the particle-based method used to describe the fluid, and molecular dynamics (MD) is employed to describe the colloids and the colloid-fluid interactions [29,30]. This description has shown to properly incorporate hydrodynamic interactions, also in phoretic systems [31–34]. MPC describes the fluid as a collection of point particles of mass $m$ that perform alternating streaming and collision steps. In the streaming step, particles propagate ballistically for a time $h$. In the collision step, the particles are binned into cells of side length $a$. A grid shifting procedure [35] is employed during this binning to ensure Galilean invariance. Inside the collision cells, the particles velocities relative to the center-of-mass velocity of the cell are rotated around a random axis by an angle $\alpha$. The choice of $a = 1, m = 1$ and $k_B T = 1$ defines the simulation units, so that time is scaled with $(ma^2/k_B T)^{1/2}$ and velocity with $(k_B T/m)^{1/2}$. The other parameters are here chosen to be $\alpha = 120^\circ$ and $h = 0.1$, together with the averaged number of particles per collision cell, $\rho = 10$. These numbers determine the fluid transport properties as the diffusion coefficient $D_s = 0.06$, the kinematic viscosity $\nu = 0.79$, or the thermal diffusivity $k_T = 0.15$ [32,34]. The resulting Prandtl number, $Pr = \nu/k_T = 5.3$, is very close to that of various fluids such as water, and enables local temperature gradients to remain stable under adequate boundary conditions. The related Schmidt number, $Sc = \nu/D_s = 13$, is smaller than that of water, but shows that the propagation of momentum is faster than that of mass, which has extensively been shown to provide a very efficient approach to include hydrodynamic interactions [33,36].

Colloid-fluid interactions are modeled with MD, and the choice of the potential is crucial to determine phoretic and thereby collective properties of the colloids. We use displaced Lennard-Jones–type potentials given by

$$U(r) = \begin{cases} \infty, & r \leq \Delta, \\ 4\varepsilon \left( \frac{\sigma}{r-\Delta} \right)^{12} - \left( \frac{\sigma}{r-\Delta} \right)^{6} + C, & \Delta < r < r_c, \\ 0, & r_c \leq r. \end{cases}$$

(1)

Here $r$ is the pairwise distance, $\varepsilon$ describes the strength of the potential which we choose as $\varepsilon = k_B T$, and $\Delta$ introduces a displacement. Repulsive interactions are obtained with $C = \varepsilon$ and $r_c = 2^{1/2}\sigma + \Delta$, and attractive with $C = 0$ and $r_c = 1.13\sigma + \Delta$. Previous simulations [37] have shown that the use of repulsive potentials results in a thermophilic behavior, while attractive interactions translate into a thermophobic behavior which is the one experimentally more frequently observed. With this model, the effective radius of each bead is $s = \sigma + \Delta$, and we denote the related size parameters as $(s, \Delta)$. Dimers investigated here are constructed by one hot bead with repulsive interactions of size $s_H$, which we mostly fix as $(6, 3)$ or $(2, 0.5)$; and one non-heated bead with attractive interactions of size $s_P$, which we fix as $(6, 3)$. We refer to the non-heated bead as the phoretic bead, since its surface experiences a thrust due to the temperature gradient of the surrounding solvent. Both beads are held together by a strong harmonic potential at a distance $s_H + s_P$. Mimicking the heating obtained by laser illumination of half gold-coated particles [9], we rescale the temperature of fluid particles in a short layer (0.08$s_H$) around the hot beads to a value of $T_h = 1.5$, while keeping the overall average fluid temperature at $T = 1.0$ using simple velocity rescaling [10,38]. This constant heating neglects shadowing effects [19], but those are expected to have small influence for the repulsive thermophoretic behavior here employed. Simulations are performed using a modified variant of the software package LAMMPS [39], in particular a modified version of the “srd”-package [40]. The time step to integrate the potential interactions is $\Delta t = 0.01h$, and the bead mass, $M$, is chosen such that the swimmers are neutrally buoyant.

**Single dimers.** – Besides the employed colloid-fluid interactions, the swimmer dimensions importantly influence both the swimmer velocity and hydrodynamic behavior. Given a constant temperature gradient, the size of the phoretic bead will determine the phoretic thrust, which will be larger, the larger the bead [37,41]. In this study the size of the phoretic bead is fixed to $s_P = 6$. The symmetric swimmer with $s_H = s_P$ shows a propelled velocity against the heated bead with an average value of $v_0 = 0.021$, which corresponds to a Reynolds number $Re = v_0 s/\nu = 0.32$, where the relevant particle size is $s = s_H + s_P$. It was observed in previous studies that such choice of Reynolds numbers, though non-zero, agrees very well with Stokes behavior where inertial effects are neglected [38]. Increasing the size of the heated bead increases the temperature gradient around the phoretic bead, thus its phoretic thrust, together with the overall friction of the swimmer. The combination of these two effects results in a maximum of the propelled swimmer velocity as a function of the size ratio $\gamma = s_P/s_H$, as can be seen in fig. 1(a). The dimer velocity is measured in the main dimer axis towards the phoretic bead. The bead size ratio of the dimer also changes its rotational diffusion coefficient which we have measured for $\gamma = 1$ as $D_r = 2.5 \times 10^{-5}$ and for $\gamma = 3$ as $D_r = 1.2 \times 10^{-4}$, what allows us to determine the Peclet number $Pe = v_0/(sD_r)$ of both swimmers as 70 and 20, respectively. These dimensionless numbers are comparable, and even a bit higher than those of experimentally synthesized spherical Janus swimmers [5,9,42]. Employing as reference the experimental Janus thermophoretic particles of 1 $\mu$m in ref. [9], a first estimation of velocities of the dimers from 20 to 200 $\mu$m s$^{-1}$ can be obtained.

The swimmer shape also influences strongly the hydrodynamic response of the surrounding fluid. The quantitative values of the flow velocities in the axis perpendicular

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to the swimmer orientations are depicted in fig. 1(b), and the stream lines around the two thermophoretic dimers are displayed in figs. 1(c), (d). Negative values of the velocity correspond to fluid streaming towards the bead (hydrodynamic attraction), while positive values correspond to the fluid streaming away from the bead (hydrodynamic repulsion). The dimers’ flow fields are of the point force-dipole type [34,43], whose precise form strongly depends on the geometry of the swimmer. Note that similar to swimmer characterized as pusher dipoles [3], thermophobic active dimers push the fluid outwards in axial direction, although the precise flow fields are more complex. Another well-known model of swimmers with a related pusher-type of behavior is the spherical squirmer model with negative squirming parameter [44,45]. The active dimers here discussed are though intrinsically different to the squirmer model, given the bispherical geometry, and the fact that the velocity slip around the colloid surface is not ad hoc imposed as in the case of the squirmers, but emerges as a consequence of the constituent dimer geometry, surface properties, and temperature boundary conditions; these being all experimentally controllable properties.

The symmetric dimer, with \( \gamma = 1 \) (see figs. 1(b), (c)), shows mainly hydrodynamic lateral repulsion, although there is a small region close to the phoretic bead where attractive interactions also exist. Such a crossover from attraction to repulsion in the lateral part is due to the complex geometry of the dimer, simpler spherical geometries do not exhibit similar features. The flow field qualitatively changes in the case of asymmetric dimers, with \( \gamma = 3 \) (see figs. 1(b), (d)), which show strong and long-ranged lateral hydrodynamic attraction. This can be seen in fig. 1(d), where the stream lines show a large attractive lobe close to the phoretic bead, and in fig. 1(b) where the fluid velocity is clearly negative over the whole range of accessible distances. These two dimers show the effect in a very pronounced way, for intermediate size ratios the attractive lobe builds up further with increasing \( \gamma \). Qualitative agreement is found with analytical results for catalytic dimers with opposite phoretic interaction [34]. However, an additionally considered separation between beads translates into the appearance of a third lobe, non-existing in our case.

Ensembles of dimers. – Interactions between active phoretic dimers are the result of several contributions, of which the phoretic and the hydrodynamic interactions are the most relevant ones. The heated bead of each dimer produces a temperature gradient in the surrounding solvent which affects, not only the attached phoretic bead, but also any other phoretic bead nearby. Thermophobic dimers, like the ones considered here, would therefore phoretically repel other thermophobic dimers at their phoretic bead. This phoretic interaction is strongest to the rear in axial direction, where the temperature field is not shielded by the phoretic bead of the same dimer, and coexists with the hydrodynamic interactions resulting from the induced flow fields. Thus, two thermophobic dimers might attract each other in the lateral direction, while simultaneously repelling each other in the axial direction. This particular interplay strongly suggests that these dimers will tend to assemble in single-layered structures, with hexagonal and high orientational order; such that they will collectively self-propel as a front. The axial phoretic repulsion hinders the attachment of dimers in the front and rear directions, being responsible of the formation of single-layered structures. The lateral hydrodynamic attraction brings these structures together and induces a certain orientational order. These predictions can be tested by characterizing the collective dimer dynamics, for which we perform simulations of thermophobic swimmers of both size ratios, with a fixed volume fraction of \( \phi = 0.05 \), having \( N = 100 \) swimmers as reference system and extending the study to various swimmers number. Colloid-colloid strong repulsive interactions are considered between all \( i, j \) beads of different dimers, by using potentials corresponding to eq. (1) with \( \Delta = 0, \epsilon = 2.5k_B T \), and \( C = \epsilon \). Particular attention has to be paid to depletion interactions between colloids, which might occur due to the high compressibility of the MPC fluid [46], and have special relevance in the case of attractive colloid-fluid interactions [47]. This artificial depletion is here completely circumvented by the choice of the colloid-fluid potential \( U(r) \) in eq. (1), and related

Fig. 1: (Color online) (a) Single swimmer velocity \( v_s \) as a function of the bead size ratio \( \gamma \) normalized by the velocity of the symmetric swimmer, \( v_s|_{\gamma=1} \). (b) Fluid velocity \( v_t \) as a function of \( r \), the distance to the center of the phoretic bead in the axis perpendicular to the swimmer orientation. The normalizing factor \( v_s|_{\gamma} \) is the corresponding single swimmer velocity. The vertical grey line is the minimum distance from the phoretic bead center to the surface of another dimer. Blue lines stand for asymmetric dimers and red for symmetric dimers. (c) Flow field characterization in the area close to the symmetric dimer \( \gamma = 1 \). Solid lines correspond to the stream lines, background color depicts the temperature field, and grey arrows show the direction of the fluid velocity. The black thick arrow indicates the dimer swimming direction. (d) Flow field close to the asymmetric dimer \( \gamma = 3 \), with symbols similar to (c). Simulations are done in a cubic periodic box of side length \( 10(s_H + s_P) \).
clusters, swimming in random directions. The other two clusters show clear orientational order, which will be necessarily accompanied by a significant average velocity. The light green structure of asymmetric dimers in fig. 2(b) and that in figs. 2(c), (d) are examples of distinct large clusters which collectively move as a front, as was to be expected from the single-particle dynamics. Note that in these snapshots a distinct degree of planar and hexagonal order is obvious, but certainly subject to considerable stochasticity. Although the two described assembling mechanisms, hydrodynamics and collisions, are present for both symmetric and asymmetric swimmers, hydrodynamics are clearly more important for the asymmetric ones. In the case of the symmetric dimers the clusters are small-sized and short-lived, while asymmetric dimers form considerably larger and faster clusters with a pronounced tendency to be planar aligned, which can propel over one to several dimer lengths. The order in the clusters is largely hindered by the stochastic nature of the system. This does not destroy, but largely diminish the planarity and hexagonal order of the swarming clusters of asymmetric dimers, as can be seen in figs. 2(c), (d). These swarming clusters can be compared with the observed behavior of the living crystals formed by spherical diffusiophoretic colloids in quasi-2D confinement [17,48], or squirmer-type swimmers [49]. All these systems show crystallization in large transient clusters, which constantly assemble and de-assemble. The crystallization and assembly dynamics is significantly different, and most remarkably, only the swarming clusters here discussed show a front-like structure with clear net propelled motion.

To better quantify these effects we perform a cluster analysis of our simulation results. Any two dimers with beads $i, j$ closer than $1.32(s_i + s_j)$ (this is 1.1 times the colloid-colloid minimum interaction distance), and for times longer than 300, are considered to belong to the same cluster. Figure 3(a) displays the probability of a dimer to be part of a cluster of size $N_c$. Although most dimers are part of very small clusters, it can be seen that for symmetric dimers a significant fraction of them assembles in clusters of up to 20 swimmers; meanwhile asymmetric dimers show to assemble in significantly larger clusters which might reach up to 150 swimmers for the larger systems. Note that once a cluster is formed, the number of constituent dimers is strongly fluctuating, since single dimers are constantly attaching and detaching, and the cluster is easily dividing and merging with others. An indication of the most typical cluster sizes can then be found in the plateaus of the probability function in fig. 3(a), which indicates $N_c = 45$ for $\gamma = 1$ and $N_c = 100$ for $\gamma = 3$. The main cluster direction is obtained by averaging all single-dimer axes $\mathbf{n}_i$, and the cluster velocity is the average of the dimer velocities projected on such cluster direction. Results for the cluster velocity are plotted in fig. 3(b); and for the average correlation of all dimer orientations in a cluster ($\mathbf{n}_i \cdot \mathbf{n}_j$) in fig. 3(c). For symmetric dimers, the velocity and the orientation clearly

parameters, together with the colloid-colloid interaction distance, $\sigma = 1.2(s_i + s_j)$. The included small additional separation also resolves lubrication forces [46] and does not interfere with the hydrodynamic interactions. With these constraints, to fully resolve hydrodynamic and phoretic interaction is computationally very costly, which strongly limits the size of the systems we can simulate, since for example we need to employ up to $10^8$ MPC fluid particles.

Ensembles of thermophobic dimers with the two considered symmetries reach a steady state characterized by a very dynamic behavior, in which the swimmers are constantly assembling and de-assembling in clusters of various sizes. Snapshots illustrating different kinds of behavior are shown in fig. 2, and two representative movies can be found in the supplemental material (SM), see Tdimers_asym_500.mp4, Tdimers_sym_100.mp4 and their description Supplementarymaterial.pdf. In fig. 2(a), four clusters of symmetric dimers can be distinguished, the two blue ones are randomly jammed structures, resulting from collisions of various dimers or existing smaller clusters, swimming in random directions. The other two clusters show clear orientational order, which will be necessarily accompanied by a significant average velocity. The light green structure of asymmetric dimers in fig. 2(b) and that in figs. 2(c), (d) are examples of distinct large clusters which collectively move as a front, as was to be expected from the single-particle dynamics. Note that in these snapshots a distinct degree of planar and hexagonal order is obvious, but certainly subject to considerable stochasticity. Although the two described assembling mechanisms, hydrodynamics and collisions, are present for both symmetric and asymmetric swimmers, hydrodynamics are clearly more important for the asymmetric ones. In the case of the symmetric dimers the clusters are small-sized and short-lived, while asymmetric dimers form considerably larger and faster clusters with a pronounced tendency to be planar aligned, which can propel over one to several dimer lengths. The order in the clusters is largely hindered by the stochastic nature of the system. This does not destroy, but largely diminish the planarity and hexagonal order of the swarming clusters of asymmetric dimers, as can be seen in figs. 2(c), (d). These swarming clusters can be compared with the observed behavior of the living crystals formed by spherical diffusiophoretic colloids in quasi-2D confinement [17,48], or squirmer-type swimmers [49]. All these systems show crystallization in large transient clusters, which constantly assemble and de-assemble. The crystallization and assembly dynamics is significantly different, and most remarkably, only the swarming clusters here discussed show a front-like structure with clear net propelled motion.

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Fig. 2: (Color online) Snapshots of ensembles of thermophoretic dimers. (a) Symmetric swimmers ($\gamma = 1, N = 100$). (b) Asymmetric swimmers ($\gamma = 3, N = 100$). Non-assembled dimers are translucent, with red heated beads and blue phoretic beads. Dimers assembled in clusters of size five or larger are solid, with red heated beads and phoretic beads colored according to cluster identity. See related movies in the SM. (c), (d): close-up snapshots corresponding to the front and side view of one large cluster in a simulation with $N = 500$ asymmetric swimmers ($\gamma = 3$).
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decay with cluster size, and although significant propulsion velocity and orientation is found for small clusters, both are almost vanishing for the largest clusters of symmetric dimers, as expected for jammed structures. For asymmetric dimers, velocities and orientations show similar initial decay, but soon this decay is much slower and it reaches a value roughly constant for clusters larger than 40 swimmers and smaller than 75, as indicated with gray lines in fig. 3(b), (c). The velocity and orientation of moving flattened clusters are though underestimated by these roughly constant values, since the averages also account for non-moving clusters formed by the collisions of smaller clusters. Simulations with \( N = 500 \) swimmers indicate that swarming clusters larger than 200 are not being formed anymore. The fact that these swarms are sufficiently smaller than the simulation box indicates that this limit does not depend on the system size, but on the stability of hydrodynamic lateral attraction as compared to both thermal fluctuations as well as an increased friction due to the planar-like geometry. On the other hand, the maximum cluster size will strongly depend on various other system parameters such as the system volume fraction, single swimmer Peclet number, or the particle geometry. To precisely quantify the degree of planarity of a cluster is in principle possible by considering its gyration tensor \([50]\). However, representative values are difficult to obtain given the dynamic and stochastic nature of the clusters. On the other hand, it can be expected that experimental realizations of this effect will display a more coherent effect since the experimental phoretic forces can be larger than those here simulated \([51]\).

Apart from the hydrodynamic and phoretic interactions, additional inter-dimer alignment is caused by the combination of self-propulsion and steric repulsion, which we here refer to as motility-induced attraction. This alignment occurs since two rod-like propelling particles stay together longer than non-propelling ones, resulting into an effective attraction, which has already been observed for elongated swimmers \([52,53]\). This effect should however be weak, as the dimers feature very low aspect ratios. To evaluate its importance, we perform Langevin Dynamics (LD) simulations, where hydrodynamics and phoretic effects are completely disregarded. Dimeric propelled particles are simulated by imposing driving forces that relate to swimming velocities comparable to those in the hydrodynamic simulations. Fluid friction is considered by an implicit solvent that we tune to lead to an effective viscosity very similar to the one in MPC-MD. Explicitly, LD considers dimers interacting with the same pairwise interaction as in MPC-MD, together with very similar propulsion, friction, and random forces. Self-propulsion in LD is included via the propulsion force \( f_p \) which is applied to the phoretic bead in the axial dimer direction \( n \), and it is proportional to the swimming velocity \( v_s \), which we obtain from the MPC-MD simulations. The propulsion force is therefore \( f_p = (\mu_h + \mu_p)v_sn \), where \( \mu_h,p \) refer to the damping coefficients of the hot and phoretic bead, respectively. These mobilities are calculated from the Einstein relation as \( \mu = 6\pi\eta s \) with \( \eta = \rho\nu \) being the dynamic viscosity of the MPC fluid. The friction force \( f_{\text{damp}} \) and the random force \( f_{\text{rand}} \) are then considered for each bead. The damping term is \( f_{\text{damp}} = -(M/\mu)v \), where \( M \) is the mass of each bead, and \( v \) its actual velocity; and the random force is given by \( f_{\text{rand}} = (2\xi B T/\mu\mu)^{1/2}\xi \), where \( \xi \) is a delta-correlated Gaussian white noise. Note that alternative methods proposed to turn off hydrodynamic interactions in MPC simulations \([54,55]\) are not useful in our case. These methods are based on randomizing the velocities of the solvent particles, which annihilates the phoretic effect, and therefore also the active character of the system. The challenge is then to find a method that, without including hydrodynamic interactions, would still account reasonably well for the phoretic effect.

Results of the LD simulations are shown in fig. 3 with dashed lines. In the LD simulations, only small, and very
short short-lived aggregates with low orientational correlation form, with nearly identical results for both considered geometries. This shows that jamming is the main clustering mechanism for LD simulations. The comparison of LD and MPC-MD simulation results offers several interesting insights. In the presence of hydrodynamic interactions, the importance of motility-induced attraction is almost negligible, and it is the form of the hydrodynamic interactions what determines the differences between asymmetric and symmetric dimers. Long-range hydrodynamic attractions of asymmetric dimers result then in their flattened swarming, while the short-ranged hydrodynamic attractions of the symmetric dimers enhance their alignment quite strongly (cf. blue lines in fig. 3(c)). The importance of short-ranged hydrodynamic interactions has also been observed in other colloidal systems [22] in a different context. Since the phoretic effect is purely repulsive and motility-induced attraction rather weak for dimers, we conclude that the only attractive interaction that may account for the swarm formation is the lateral hydrodynamic attraction.

Conclusion. – The hydrodynamic assembly of ordered, flattened, moving fronts in three dimensions seems to be specific to systems of asymmetric dimeric swimmers driven by repulsive phoresis, since no comparable behavior has yet been observed in other synthetic or biological active systems [3,45,56,57]. Given the feasibility of synthesizing these structures [6] it is to be expected that they will be soon experimentally investigated. Our simulation studies provide a first proof of concept for the emergence of this swarming behavior in phoretic colloidal systems, and show how the underlying physical mechanism is based on the combination of axial phoretic repulsion and lateral hydrodynamic attraction. Further insight into the phenomenology will be obtained when extending this study for example to other volume fractions, or bead size ratios. The scope of possible applications of active matter is broadened by the phenomenon of front-like swarming, which offers new possibilities for example in the design of microfluidic devices or bio-compatible micromotors.

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