Conspectus

Diffusion is the principal transport mechanism that controls the motion of solute molecules and other species in solution; however, the random walk process that underlies diffusion is slow and often nonspecific. While diffusion is an essential mechanism for transport in the biological realm, biological systems have devised more efficient transport mechanisms using molecular motors. Most biological motors utilize some form of chemical energy derived from their surroundings to induce conformational changes in order to carry out specific functions. These small molecular motors operate in the presence of strong thermal fluctuations and in the regime of low Reynolds numbers where viscous forces dominate inertial forces. Thus, their dynamical behavior is fundamentally different from that of macroscopic motors and different mechanisms are needed to produce useful mechanical motion.

There is no reason why the use of small motors should be confined to naturally occurring biological systems. Recently, micron and nano-scale motors that use chemical energy to produce directed motion by a number of different mechanisms have been made in the laboratory. These small synthetic motors also experience strong thermal fluctuations and operate in regimes where viscous forces dominate. Potentially, these motors could be directed to perform different transport tasks, analogous to those of biological motors, for both in vivo and in vitro applications. While some synthetic motors execute conformational changes to effect motion, the majority do not and, instead, they use other mechanisms to convert chemical energy into directed motion.

In this Account we describe how synthetic motors that operate by self-diffusiophoresis make use of a self-generated concentration gradient to drive motor motion. A detailed description of propulsion by self-diffusiophoresis is presented for Janus particle motors comprising catalytic and noncatalytic faces. The properties of the dynamics of chemically-powered motors are illustrated by presenting the results of particle-based simulations of sphere-dimer motors constructed from linked catalytic and noncatalytic spheres. The geometries of both Janus and sphere-dimer motors with asymmetric catalytic activity support the formation of concentration gradients around the motors. Since directed motion can only occur when the system is not in equilibrium, the nature of the environment and the role it plays in motor dynamics is described. Rotational Brownian motion also acts to limit directed motion and it has especially strong effects for very small motors. We discuss just how
small motors can be made and yet still exhibit effects due to propulsion, even if only to enhance diffusion. Synthetic motors have the potential to transform the manner in which chemical dynamical processes are carried out for a wide range of applications.

Introduction

A large effort has been made in recent years to synthesize and study micron and nano-scale motors and machines. These small devices are constructed from a wide range of materials, such as DNA, polymers, or metals, take many different shapes and sizes and, owing to such variety, are able to move using different mechanisms. They have been shown to act, at least in proof-of-concept, as walkers, shuttles, rotors, pumps, cargo-carriers, muscles and artificial flagella and cilia. Some synthetic motors are designed to move as a result of nonreciprocal cyclic conformational changes, mimicking many of the motors and microorganisms found in nature. Motors that do not rely on conformational changes for motion have also been constructed, and these motors are the principle focus of this Account.

Apart from nanomotors without moving parts that are propelled by external stimuli, many such motors rely on chemical reactions for propulsion. The fuel they use is not carried by the motor itself but, rather, it is derived from the local environment: they are active devices that use the chemical energy available in their immediate vicinity to perform work. In place of asymmetrical conformational changes, these chemically-powered motors are constructed with a structural asymmetry in chemical activity that leads to directed motion. The motor motion depends on the characteristics of both the motor and its environment, and their interaction with one another.

The first chemically-propelled nanomotors were bimetallic rods constructed with gold and platinum or nickel portions, which, when placed in solutions containing hydrogen peroxide, were able to execute autonomous linear and rotational motions. Subsequently, other types of chemically-driven motors were synthesized. Similar to bimetallic rods, these motors contain two main domains that are composed of different materials, allowing for chemical reactions to occur asymmetrically on the motor. Janus particles are spherical colloids generally made from one material, half covered by another material, giving the appearance of two faces. Sphere-dimer motors are similar to Janus particles, but instead comprise two linked spheres made of different materials. Microtubular motors are hollow cylindrical or conical tubes that have a reactive interior and inert exterior. While many of these motors rely on the same platinum-peroxide catalytic reaction, motors constructed more recently have incorporated different metals, alloys, or compounds, in order to provide better control over motion or to exploit different fuels.

Regardless of the specific motor geometry or fuel, two classes of mechanisms are largely responsible for the self-propulsion of chemically-driven nanomotors. Bubble propulsion is due to the catalytic production of gas at the motor and the resulting recoil of the gas bubbles from the motor surface. This mechanism is usually invoked whenever bubbles are directly observed, as is the case with tubular motors, where gas accumulates in the motor interior and is expelled from one of the ends. In phoretic mechanisms the motor self-generates some type of gradient (electrical, concentration, temperature) in its vicinity through a chemical reaction, and motion is induced by this gradient. For bimetallic rod motors a flow of electrons in the rod between the anodic and cathodic sites of a redox reaction creates a self-generated electric field that drives ion motion in the electrical double layer surrounding the motor. In some situations more than one phoretic mechanisms may operate for the same motor. For example, the mechanism by which sphere dimers move is highly dependent on the rate of catalysis and surface roughness, and may move either by bubble propulsion or self-diffusiophoresis. Both self-electrophoretic and diffusiophoretic mechanisms have been shown to contribute to the propulsion of the same motor. Simulations of Janus particles fueled by exothermic reactions have also shown that self-diffusiophoresis and self-thermophoresis may act at the same time, and possibly in opposite directions.
Figure 1: A Janus particle, in the laboratory frame of reference, which is self-propelled by a diffusiophoretic mechanism. The catalytic part (red, upper hemisphere) catalyzes the conversion of the fuel $A$ (not shown) to the product $B$ (purple). The chemically inactive face is the lower (blue) hemisphere. The dipolar fluid velocity field in the particle vicinity is also shown (green lines).

**Chemically-powered motors**

The means by which small motors use chemical reactions to execute directed motion may be illustrated by considering a spherical Janus particle with catalytic and noncatalytic faces, which is shown in Fig. 1. The fluid surrounding the particle contains solvent, $S$, fuel $A$ and product $B$ chemical species. The chemical reaction $A \rightarrow B$ takes place on the catalytic face of the Janus particle.

The molecular origin of propulsion can be traced to the different interactions that the fuel and product molecules have with the Janus particle. The intermolecular potentials are assumed to be short ranged and take non-zero values only within a thin interfacial region surrounding the Janus particle (dashed line in Fig. 1). Since the catalytic activity is confined to one face of the particle, a non-uniform distribution of fuel and product molecules is produced in its vicinity. The resulting concentration gradient gives rise to a force on the Janus particle. Because there are no external forces acting on the system and the intermolecular forces are short ranged, the Janus particle plus the solvent within the boundary layer is force-free. Through momentum conservation a flow is generated in the surrounding fluid and the particle is propelled in a direction opposite to the fluid flow.

In more quantitative terms, the fluid flow in the boundary region leads to a slip velocity, $v_s$, on its outer edge at $r = R_0$, whose value depends on the concentration gradient, intermolecular forces and solvent viscosity through the relation,\(^18,19\)

$$v_s(R_0, \theta) = \frac{k_B T}{\eta} (\Lambda_N + (\Lambda_C - \Lambda_N) H(\theta)) \nabla \theta c_A(R_0), \quad (1)$$

where $\theta$ is the polar angle in a spherical polar coordinate system, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $c_A$ is the concentration of the $A$ molecules, and $H(\theta)$ is a characteristic function that is unity on the catalytic hemisphere ($0 \leq \theta \leq \pi/2$) and zero on the noncatalytic $N$ hemisphere ($\pi/2 < \theta \leq \pi$).\(^3,20\) In this equation the intermolecular potentials enter through $\Lambda_I$,

$$\Lambda_I = \int_0^\infty dr \ r \left( e^{-\beta U_{\alpha I}(r)} - e^{-\beta U_{A}(r)} \right), \quad (2)$$

where $\beta = 1/(k_B T)$ and $U_{\alpha I}$ is the potential of mean force between the chemical species $\alpha$ ($\alpha = A, B$) and the $I$ ($I = C, N$) hemisphere of the Janus particle. The velocity of the Janus particle is given in terms of the surface ($\Sigma$) average of the slip velocity as $\mathbf{V} = - \left< \mathbf{v}_s \right>$, where $\left< \mathbf{v}_s \right> = \iint_{\Sigma} \mathbf{v}_s \, d\Sigma/(4\pi R_0^2)$.

The concentration field of the $A$ molecules is found by solving the steady state diffusion equation, $\nabla^2 c_A = 0$, subject to a reflecting boundary condition on the noncatalytic portion of the surface at $R \approx R_0$ and a “radiation” boundary condition on the catalytic surface: $(\mathbf{D} \cdot \nabla c_A)_{r=R} = \hat{k}_0 c_A(R) H(\theta)$, where $D$ is the relative diffusion constant of $A$ and the Janus particle, $\mathbf{r}$ is the unit vector along $r$, $\hat{k}_0 = k_0/(4\pi R^2)$, and $k_0$ is the intrinsic reaction rate constant. Far from the particle we assume there exists only fuel with concentration $c_0$ so $c_A(r \rightarrow \infty) = c_0$. The Janus particle velocity is found by substituting the concentration field obtained from the solution of the diffusion equation in the slip-velocity equation and then taking the surface average as indicated above.

It is instructive to consider the expressions for the motor velocity in two limiting cases. In the reaction-controlled limit ($k_0 \ll k_D = 4\pi RD$), we
have

\[ V_z = \frac{k_B T c_0}{8 \eta D} (\Lambda_C + \Lambda_N) \bar{k}_0, \]  

(3)

where \( V_z = \hat{z} \cdot \mathbf{V} \) and \( \hat{z} \) is the unit vector from the center of the Janus particle to the pole of the catalytic hemisphere. In the diffusion-controlled limit \( (k_0 \gg k_D) \),

\[ V_z = \frac{k_B T c_0}{\eta R} \left[ (\Omega - \Xi) \Lambda_C + (\Omega + \Xi) \Lambda_N \right], \]  

(4)

where \( \Omega \) and \( \Xi \) are the coefficients that are determined from the solution of the diffusion equation. We see from these expressions that when the reactions that occur on the catalytic part of the surface are fast compared to the diffusion of chemical species \( (k_0 \gg k_D) \), the propulsion velocity decreases with an increase in the sphere size. However, when the reaction takes place slowly \( (k_0 \ll k_D) \), the propulsion velocity does not depend on the particle size. Instead, the propulsion velocity increases as the rate of chemical reaction increases and the diffusion constant of the fuel decreases.

The fluid flow outside the interfacial layer can be calculated from the solution to the Stokes equation, and in the laboratory frame of reference it is given by

\[ \mathbf{v}(\mathbf{r}) = \frac{1}{2} (R/r)^3 (3\mathbf{r}\mathbf{r} - I) \cdot \mathbf{V}. \]  

The fluid-flow lines around the self-propelled Janus particle are shown in Fig. 1. The dipolar form of these flow lines implies a \( 1/r^3 \) decay of the velocity field far from the particle.

Another simple motor geometry consists of two linked catalytic and noncatalytic spheres (see Fig. 2). Extensive simulation studies of the dynamics of such sphere-dimer motors have been carried out under a variety of conditions; for example, in confined flows, subject to external forces, and in active media. An analysis similar to that described above for Janus particles, but technically more involved, can be carried out for these motors to obtain the velocity. Our examples of chemically-powered motor dynamics, which are given in the next section, will be confined to these sphere-dimer motors but most of the phenomena we describe are not restricted to this particular motor geometry.

Similar analyses can be carried out for propulsion by other self-phoretic mechanisms, although some details of the calculation differ. It is important to recognize that our Janus particle example was idealized and in applications to motor motion in the laboratory other factors may need to be taken into account. For bimetallic rod and Janus particle motors that operate by self-electrophoresis, the precise nature of the oxidation and reduction reactions that take place on the motor will influence its dynamics. Also, as discussed earlier, several mechanisms may simultaneously contribute to the propulsion of a motor.

**Nanomotor dynamics**

Small chemically-propelled motors are strongly influenced by fluctuations arising from interactions with the environment in which they move. In addition, as the motor size decreases to nanometer scales the validity of macroscopic models for the dynamics should be examined to determine their applicability. For these reasons it is appropriate to consider descriptions of motor motion that treat the reactive species and solvent as molecular or coarse-grained-molecular entities. In such particle-based descriptions the dynamics of
the entire system is described by either molecular dynamics or mesoscopic dynamical schemes that retain the important features of full molecular dynamics. It is especially important to preserve momentum conservation for the reasons described earlier. The results that follow were derived from simulations using hybrid molecular dynamics (MD)-multiparticle collision dynamics (MPCD)\textsuperscript{26–29} or full MD, depending on the size of the motor being studied.

Before presenting results, we note that self-propulsion can occur only under nonequilibrium conditions since detailed balance prohibits directed motion in an equilibrium system. If an excess of fuel over its equilibrium value is supplied initially, propulsion may be observed in a transient (perhaps long) time period but finally such motion will cease. For sustained motion to occur the system must be maintained in a nonequilibrium state by fluxes of reagents at the boundaries or by bulk reactions that are themselves forced out of equilibrium. Nanomotor dynamics has been studied under both types of nonequilibrium conditions.

The characteristic features of self-propelled nanomotor motion in a fluctuating environment can be seen in the trajectory of a sphere-dimer motor in Fig. 3. The motor propagates with average velocity \( V_z \) directed along the internuclear axis of the dimer. Due to rotational Brownian motion the orientation of the dimer axis changes; therefore, so does the propagation direction. For many applications, motors must be designed so as to increase their propagation speed, and methods must be imposed to overcome the influence of Brownian motion in order to control the direction in which they move. The effects of fluctuations on motor motion will be discussed in detail in the next section.

In the biological realm, molecular motors operate in complex nonequilibrium environments where the surrounding medium supports networks of chemical reactions that supply fuel and remove product. Synthetic chemically-powered motors may also operate in such complex chemical media and we present some examples to illustrate the new phenomena that arise in such situations.

Consider a sphere-dimer motor where the reaction \( A \rightarrow B \) on the catalytic sphere generates the chemical gradient responsible for propulsion. The medium in which the motor moves supports the nonequilibrium cubic autocatalytic reaction, \( B + 2A \rightarrow 3A \), where \( A \) is the autocatalyst.\textsuperscript{30} Notice that the bulk reaction consumes the product and regenerates the fuel so that motor motion may be sustained. This bulk reaction also supports the formation of a traveling chemical wave: if initially half of the system is filled with \( A \) species and the other half with \( B \), the autocatalyst will consume the \( B \) particles at the interface between these two regions leading to the formation of a propagating front. A sphere-dimer motor placed in the fuel-rich \( A \) domain and oriented towards the interface will encounter the front provided its speed is greater than that of the front. Since beyond the front the system is rich in product \( B \), the motor cannot penetrate deeply into this fuel-poor region. Instead the motor is reflected from the front (see Fig. 4). This feature suggests the possible control of motor motion by chemical patterns.

The medium in which the motor moves can support even more complex nonequilibrium oscillatory states. Oscillatory dynamics is commonly observed in biological systems where coupled autocatalytic reactions give rise to the oscillatory behavior. To study motor dynamics in such media we again suppose that the reaction on the catalytic sphere of the sphere-dimer motor is \( A \rightarrow B \). These species are also involved in bulk nonequi-
equilibrium reactions whose kinetics is controlled by the Selkov model: $S \rightleftharpoons A$, $A + 2B \rightleftharpoons 3B$, $B \rightleftharpoons S$, where $S$ is considered to be an inert feed for $A$ and $B$. The rate constants in these reactions can be chosen to yield an oscillatory state. The Selkov model has its antecedents as a simple model for glycolytic oscillations. Since the reaction on the dimer motor involves the same chemical species, it locally perturbs the Selkov oscillatory dynamics. In particular, the concentration of the product $B$ species is observed to oscillate around a higher average value close to the catalytic sphere, while the opposite trend is seen for the fuel $A$ concentration. (see Fig. 5). These shifts in the concentration cycles also create oscillations in the concentration gradient across the noncatalytic sphere, which lead to oscillations in the sphere dimer’s velocity. Thus, the motor is able to influence the local chemical kinetics of an oscillatory medium and, in turn, these changes modify the motor motion.

For the final example of nanomotor dynamics we briefly describe some aspects of the collective motion of sphere-dimer motors. Several factors have to be taken into account when the dynamics of an ensemble of chemically-powered motors is considered. Each self-propelled motor generates its own concentration gradient. If there are no bulk reactions the concentration fields will decay as the reciprocal of the distance from the motor. If there are bulk reactions that consume the product this decay may be screened but can nevertheless extend over a considerable distance. This gives rise to a chemotactic response which typically causes motors to be attracted to each other, analogous in some respects to the chemotactic response of bacteria to high food concentrations. The chemotactic response of synthetic nanomotors to chemical gradients has been observed in experiments. In addition, as discussed earlier, each motor induces a flow field in the surroundings and one motor can perturb the flow field of its neighbors. This leads to a hydrodynamic coupling among motors. The motors may also interact directly through short or long range interactions. As a consequence of all of these interactions the collective dynamics may be complicated.

The collective motion of chemically-powered nanomotors has been studied experimentally and theoretically. Phenomena, such as active self assembly and swarming, have been observed. Our earlier studies of the collective behavior of sphere-dimer motors exhibited these phenomena and confirmed the important role of coupling through chemical gradients. Here we briefly describe a more complicated system of an ensemble of two different kinds of sphere-dimer motor, termed type I and type II, which interact through chemical gradients in the following way: the product of a type I of motor is the fuel for a type II motor. In particular, type I motors catalyze the reaction $A \rightarrow B$, while type II motors catalyze the reaction $B \rightarrow C$. This is an example of a system where the motors themselves participate in networks of chemical reactions. If the system is supplied with fuel $A$, motors of type II will not actively move.
Fluctuations and diffusion

We observed earlier that while the chemical concentration gradient generated by the motor determines its propagation direction and affects its speed, orientational Brownian motion will change the direction in which it moves so that on sufficiently long times scales the directed motion will manifest itself as enhanced diffusion. The enhanced diffusion is evident from a comparison of the two trajectories in Fig. 3 corresponding to chemically active and inactive dimers. Only for times less than the orientational time will the ballistic motion of the motor be evident. A number of important questions arise when the effects of fluctuations on motor dynamics are considered. How far, on average, does the motor move before the ballistic motion is masked by Brownian motion? How is the diffusion coefficient modified by directed motion? What is the lower limit on the size of the motor for self-diffusiophoresis to operate? For micron and large nano-scale motors the answers to these questions will determine how effectively the motor can carry out transport tasks and what control scenarios must be implemented to overcome the effects of rotational Brownian motion. If such motors are ever to be used on scales comparable to the interior of a cell, it is important to determine if they can be made to operate when they are only a few nanometers in size.

The mean square displacement (MSD), $\Delta L^2(t)$, of the center of mass of the motor provides some information that can be used to answer these questions. Writing $\mathbf{V}(t) = \langle V_z \rangle \hat{z}(t) + \delta \mathbf{V}(t)$ and assuming exponential decay for the orientational $\langle \hat{z}(t) \cdot \hat{z} \rangle = e^{-t/\tau_r}$ and velocity fluctuation $\langle \delta \mathbf{V}(t) \cdot \delta \mathbf{V} \rangle = (3 k_B T / M_m) e^{-t/\tau_v}$ correlation functions, the MSD takes the form

$$\Delta L^2(t) = 6D_m t - 2\langle V_z \rangle^2 \tau_r^2 \left(1 - e^{-t/\tau_r}\right) - \frac{6 k_B T}{M_m} \tau_v^2 \left(1 - e^{-t/\tau_v}\right).$$

The effective dimer diffusion coefficient is $D_m = D_0 + \frac{1}{3} \langle V_z \rangle^2 \tau_r$, where $D_0 = (k_B T / M_m) \tau_v$. In the ballistic regime, $t \ll \tau_v$, $\Delta L^2(t) \approx (3 k_B T / M_m + \langle V_z \rangle^2) t^2$.

The majority of research has been carried out on chemically self-propelled motors with linear dimensions of microns or hundreds of nanometers, similar to those of many swimming microorganisms. Typical motor velocities are in the range of tens of micrometers per second but could be even higher. Given the motor speeds and sizes, and the kinematic viscosity of water, this places these motors in the low Reynolds number regime. Such micron-scale motors will be useful for a wide range of applications.

If one scales down by two to three orders of magnitude to the regime where motor linear dimen-
Figure 7: Mean square displacements of inactive and reactive Ångström-scale and nano-scale sphere dimers. The points show simulation data and the solid lines show theoretical predictions. The vertical dashed lines indicate crossover times between the short-time ballistic and the long-time diffusive regimes. The data is shown in dimensionless time and length units of $\tau = \sigma \sqrt{M_m/k_B T}$ and $\sigma = \sqrt{d_C^3 + d_N^3}$, respectively.

The rescaled MSDs of the inactive dimers—their motion is subject only to thermal fluctuations—is approximately equal and thus independent of the length scale. The rescaled MSD of the reactive dimers, however, reveals significant differences depending on the length scale. In the ballistic regime, $t \ll \tau$, the MSD of the reactive nanodimer is significantly larger than that of the inactive nanodimer, since the thermal velocity $\sqrt{k_B T/M_m}$ is negligible compared to the average propulsion velocity $\langle V_z \rangle$, and $\Delta L^2_m(t) \approx \langle V_z \rangle^2 \tau^2$. The MSD of the reactive Ångström-dimer, however, is almost equal to that of the inactive Ångström-dimer, since now the propulsion velocity is negligible compared to the thermal velocity, and $\Delta L^2_m(t) \approx 3k_B T/M_m \tau^2$. In the diffusive regime, $t \gg \tau$, both the reactive Ångström-dimer and the reactive nanodimer exhibit enhanced diffusion, where the enhancement is smaller (but still significant) for the Ångström-dimer as expected due to the stronger thermal fluctuations. The crossover regime from the ballistic to the diffusive regime is short for the nanodimer; for the Ångström-dimer, however, the crossover regime spans three orders in magnitude in (rescaled) time. Given $\langle V_z \rangle$ and $\tau$, the average linear distance travelled by a motor can be estimated as $\langle V_z \rangle \tau$. The reactive nanodimer travels an average distance of 11.6 times its effective diameter, $\sigma$; the Ångström-dimer travels 3.0 times its effective diameter. Thus, chemically-powered motors can operate on very small length scales and yield substantially enhanced diffusion coefficients, consistent with recent experiments on active enzymes and small Janus-like particles. These observations suggest possible applications using very small synthetic motors.

Conclusions

Investigations of very small chemically-powered motors present challenges for experiment and theory. They may also provide a diverse and transformative range of tools for new applications. Experimental challenges center around the design and construction of micron and nanoscale motors with specific geometries, fueled by various chemicals, operating by propulsion and control mechanisms selected for specific purposes. Since motors that might be used for some tasks may
be very small, continuum descriptions, while often applicable on surprisingly small length and time scales, may nevertheless break down, and this breakdown necessitates the use of microscopic or mesoscopic theories of the dynamics. Self-propelled motors function under nonequilibrium conditions and their full statistical mechanical description must account for the fluxes that drive the system out of equilibrium. In far-from-equilibrium regimes systems display features, such as bistability, oscillations and self-propulsion, that are distinct from those of equilibrium systems. The statistical mechanics of driven nonequilibrium systems is a topic of current research and complete studies of chemically-powered motors within this context have not yet been carried out.

The potential uses of nanomotors have been discussed often in articles and reviews and proof-of-principle experiments have shown that operations, such as cargo transport and motor-aided microfluidic flows, may soon lead to viable applications. Other applications, particularly those that involve biological systems, will require the development of motors that use bio-compatible fuels and motor components. In most cases a single nanomotor is insufficient to complete a task. A full understanding of the factors that lead to the collective behavior of motors, the spatio-temporal structures that develop, and methods needed to control ensembles of interacting motors must be achieved before many applications can be carried out. When such issues concerning motor design and control are completely understood it is possible that synthetic motors and active transport will play as significant a role as molecular motors and machines currently play in living systems.

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References

1 Kay, E. R.; Leigh, D. A.; Zerbetto, F. Synthetic Molecular Motors and Mechanical Machines. Angew. Chem. Int. Ed. 2007, 46, 72–191.

2 Wang, J. Nanomachines: Fundamentals and Applications; Wiley-VCH: Weinheim, 2013.

3 Kapral, R. Perspective: Nanomotors without moving parts that propel themselves in solution. J. Chem. Phys. 2013, 138, 020901.

4 Paxton, W. F.; Kistler, K. C.; Olmeda, C. C.; Sen, A.; Angelo, S. K. S.; Cao, Y.; Mallick, T. E.; Lammert, P. E.; Crespi, V. H. Catalytic Nanomotors: Autonomous Movement of Striped Nanorods. J. Am. Chem. Soc. 2004, 126, 13424–13431.

5 Fournier-Bidoz, S.; Arsenault, A. C.; Manners, I.; Ozin, G. A. Synthetic self-propelled nanorotors. Chem. Commun. 2005, 441–443.

6 Wang, W.; Duan, W.; Ahmed, S.; Mallick, T. E.; Sen, A. Nano Today 2013, 8, 531–554.

7 Howse, J. R.; Jones, R. A. L.; Ryan, A. J.; Gough, T.; Vafabakhsh, R.; Golestanian, R. Self-Motile Colloidal Particles: From Directed Propulsion to Random Walk. Phys. Rev. Lett. 2007, 99, 048102.

8 Rückner, G.; Kapral, R. Chemically Powered Nanodimers. Phys. Rev. Lett. 2007, 98, 150603.

9 Valadares, L. F.; Tao, Y.-G.; Zacharia, N. S.; Kitaev, V.; Galembeck, F.; Kapral, R.; Ozin, G. A. Nanomotors: Self-Propelled Sphere Dimers. Small 2010, 6, 565–572.

10 Mei, Y.; Huang, G.; Solovev, A.; Ureña, E. B.; Mönch, I.; Ding, F.; Reindl, T.; Fu, R.; Chu, P.; Schmidt, O. Versatile Approach for Integrative and Functionalized Tubes by Self-Assembly on Polymers. Adv. Mater. 2008, 20, 4085–90.

11 Soler, L.; Magdanz, V.; Fomin, V. M.; Sanchez, S.; Schmidt, O. G. Self-Propelled Micromotors for Cleaning Polluted Water. ACS Nano 2013, 7, 9611–9620.
12 Zhao, G.; Ambrosi, A.; Pumera, M. Clean room-free rapid fabrication of roll-up self-powered catalytic microengines. *J. Mater. Chem. A* 2014, 2, 1219–1223.

13 Wang, Y.; Hernandez, R. M.; Jr., D. J. B.; Bingham, J. M.; Kline, T. R.; Sen, A.; Mallouk, T. E. Bipolar Electrochemical Mechanisms for the Propulsion of Catalytic Nanomotors in Hydrogen Peroxide Solutions. *Langmuir* 2006, 22, 10451–10456.

14 Wang, S.; Wu, N. Selecting the Swimming Mechanisms of Colloidal Particles: Bubble Propulsion versus Self-Diffusiophoresis. *Langmuir* 2014, 30, 3477–3486.

15 Ebbens, S.; Gregory, D. A.; Dunderdale, G.; Howse, J. R.; Ibrahim, Y.; Liverpool, T. B.; Golestanian, R. Electrokinetic effects in catalytic platinum-insulator Janus swimmers. *EPL* 2014, 106, 58003.

16 Brown, A.; Poon, W. Ionic effects in self-propelled Pt-coated Janus swimmers. *Soft Matter* 2014, 10, 4016–4027.

17 de Buyl, P.; Kapral, R. Phoretic self-propulsion: a mesoscopic description of reaction dynamics that powers motion. *Nanoscale* 2013, 5, 1337–1344.

18 Anderson, J. L. Transport Mechanisms of Biological Colloids. *Ann. N. Y. Acad. Sci.* 1986, 469, 166–177.

19 Anderson, J. L. Colloid Transport by Interfacial Forces. *Ann. Rev. Fluid Mech.* 1989, 21, 61–99.

20 Golestanian, R.; Liverpool, T. B.; Ajdari, A. Designing phoretic micro- and nanoswimmers. *New J. Phys.* 2007, 9, 126.

21 Tao, Y.-G.; Kapral, R. Design of chemically propelled nanodimer motors. *J. Chem. Phys.* 2008, 128, 164518.

22 Tao, Y.-G.; Kapral, R. Dynamics of chemically powered nanodimer motors subject to an external force. *J. Chem. Phys.* 2009, 131, 024113.

23 Tao, Y.-G.; Kapral, R. Swimming upstream: self-propelled nanodimer motors in a flow. *Soft Matter* 2010, 6, 756–761.

24 Thakur, S.; Kapral, R. Dynamics of self-propelled nanomotors in chemically active media. *J. Chem. Phys.* 2011, 135, 024509.

25 Popescu, M. N.; Tasinkevych, M.; Dietrich, S. Pulling and pushing a cargo with a catalytically active carrier. *EPL* 2011, 95, 28004.

26 Malevanets, A.; Kapral, R. Mesoscopic model for solvent dynamics. *J. Chem. Phys.* 1999, 110, 8605–8613.

27 Malevanets, A.; Kapral, R. Solute molecular dynamics in a mesoscale solvent. *J. Chem. Phys.* 2000, 112, 7260–7269.

28 Kapral, R. Multiparticle Collision Dynamics: Simulation of Complex Systems on Mesoscales. *Adv. Chem. Phys.* 2008, 140, 89–146.

29 Gompper, G.; Ihle, T.; Kroll, D.; Winkler, R. In Advanced Computer Simulation Approaches for Soft Matter Sciences III; Holm, C., Kremmer, K., Eds.; Adv. Polym. Sci.; Springer Berlin Heidelberg, 2009; Vol. 221; pp 1–87.

30 Thakur, S.; Chen, J.-X.; Kapral, R. Interaction of a Chemically Propelled Nanomotor with a Chemical Wave. *Angew. Chem. Int. Ed.* 2011, 50, 10165–10169.

31 Berg, H. C. *E. coli in Motion*; Springer-Verlag: New York, 2004.

32 Hong, Y.; Blackman, N. M. K.; Kopp, N. D.; Sen, A.; Velegol, D. Chemotaxis of Nonbiological Colloidal Rods. *Phys. Rev. Lett.* 2007, 99, 178103.

33 Baraban, L.; Harazim, S. M.; Sanchez, S.; Schmidt, O. G. Chemotactic Behavior of Catalytic Motors in Microfluidic Channels. *Angew. Chem. Int. Ed.* 2013, 125, 5662–5666.

34 Theurkauff, I.; Cottin-Bizonne, C.; Palacci, J.; Ybert, C.; Bocquet, L. Dynamic Clustering in Active Colloidal Suspensions with Chemical Signaling. *Phys. Rev. Lett.* 2012, 108, 268303.
35 Buttinoni, I.; Bialké, J.; Kümmel, F.; Löwen, H.; Bechinger, C.; Speck, T. Dynamic Clustering and Phase Separation in Suspensions of Self-Propelled Colloidal Particles. *Phys. Rev. Lett.* **2013**, *110*, 238301.

36 Thakur, S.; Kapral, R. Collective dynamics of self-propelled sphere dimer motors. *Phys. Rev. E* **2012**, *85*, 026121.

37 Soto, R.; Golestanian, R. Self-Assembly of Catalytically Active Colloidal Molecules: Tailoring Activity Through Surface Chemistry. *Phys. Rev. Lett.* **2014**, *112*, 068301.

38 Lee, T.-C.; Alarcón-Correa, M.; Miksch, C.; Hahn, K.; Gibbs, J. G.; Fischer, P. Self-Propelling Nanomotors in the Presence of Strong Brownian Forces. *Nano Lett.* **2014**, *14*, 2407–2412.

39 Pavlick, R. A.; Dey, K. K.; Sirjoosingh, A.; Benesi, A.; Sen, A. A catalytically driven organometallic molecular motor. *Nanoscale* **2013**, *5*, 1301–1304.

40 Colberg, P. H.; Kapral, R. Ångström-scale chemically powered motors. *EPL* **2014**, *106*, 30004.

41 Muddana, H. S.; Sengupta, S.; Mallouk, T. E.; Sen, A.; Butler, P. J. Substrate Catalysis Enhances Single-Enzyme Diffusion. *J. Am. Chem. Soc.* **2010**, *132*, 2110–2111.

42 Sengupta, S.; Dey, K. K.; Muddana, H. S.; Tabouillot, T.; Ibele, M. E.; Butler, P. J.; Sen, A. Enzyme Molecules as Nanomotors. *J. Am. Chem. Soc.* **2013**, *135*, 1406–1414.