Osmotic Propulsion: The Osmotic Motor

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(Received 14 March 2007; published 17 April 2008)

A model for self-propulsion of a colloidal particle—the osmotic motor—immersed in a dispersion of "bath" particles is presented. The nonequilibrium concentration of bath particles induced by a surface chemical reaction creates an osmotic pressure imbalance on the motor causing it to move. The ratio of the speed of reaction to that of diffusion governs the bath particle distribution which is employed to calculate the driving force on the motor, and from which the self-induced osmotic velocity is determined. For slow reactions, the self-propulsion is proportional to the reaction velocity. When surface reaction dominates over diffusion the osmotic velocity cannot exceed the diffusive speed of the bath particles. Implications of these features for different bath particle volume fractions and motor sizes are discussed. Theoretical predictions are compared with Brownian dynamics simulations.

The design of nanoengines that convert stored chemical energy into motion is a key challenge of nanotechnology, especially for engines that can operate autonomously [1]. Although biomolecular motors [2] and phoretic mechanisms [3] have been the focus of intense research as a means for powering nanodevices, many of the proposed techniques rely on external forcing or signaling, which adds complexity, not to mention the macro-scale size required for some driving mechanisms. Recently, Paxton *et al.* [4] demonstrated that it is possible to power the motion of nanoscale objects by using surface catalytic reactions—so-called catalytic nanomotors.

A number of mechanisms have been suggested for nanomotor propulsion [5,6], including bubble propulsion, diffusiophoresis, electrophoresis, surface-tension gradients, etc.; all of which rely on the establishment of a gradient to provide the driving force for motion. Creation of such a gradient requires an on-board power source—chemical energy. But exactly how does a local chemical reaction generate motion? Or asked differently, what is the simplest motor one can envision? What mechanism would it use for propulsion? How fast can it move? How large of a force can it generate?

Here we propose a very simple mechanism: osmotic propulsion. When a semipermeable membrane separates a fluid containing colloidal particles, a flow is induced from the low to the high particle concentration side. The pressure that stops the flow is the osmotic pressure. If the membrane is released, the osmotic pressure difference between the two sides will cause it to move until equilibrium is established. In this way the microscopic kinetic energy of the (Brownian) particles is transformed into macroscopic mechanical motion and work.

But one does not need a membrane. A colloidal particle in solution moves randomly, but if the distribution of other colloidal particles in its vicinity is perturbed, some average directional movement can be obtained. Such is the case in multicomponent diffusion where a gradient in concentration of one species drives the flux of another [7,8]. Similarly, depletion flocculation occurs when small particles (e.g., polymers) are excluded from a zone separating two nearly touching colloidal particles and the imbalanced osmotic pressure of the small particles causes an entropic attractive force [9]. Consider now a nonuniform concentration distribution of colloidal particles created locally by a surface chemical reaction on another (larger) particle. The resulting imbalanced osmotic force will induce autonomous motion—an osmotic motor. This is a simple means by which random entropic motion can be harnessed by a chemical reaction to create directed motion. Just how large a force can be generated and how fast an object can move is the subject of this Letter.

Consider a single spherical motor particle of size a immersed in a fluid and surrounded by a sea of spherical "bath" particles of size b. Both the motor and bath particles are large compared to the solvent molecules so that their behavior can be described by the equations of colloidal dynamics [10]. The suspension of bath particles generates an osmotic pressure $\Pi = n_b kT$, where kT is the thermal energy and n_b is the number density of bath particles. (For simplicity, the bath particles are modeled as an ideal gas.) The bath particles exert an entropic or osmotic force on the motor, which is the integral of the osmotic pressure over the surface of the motor: $\boldsymbol{F}^{\text{osm}} = -kT \int \boldsymbol{n} n_b(\boldsymbol{x}) dS$, where $\boldsymbol{n}$ is the outer normal to the surface located at the sum of the radii of the motor and the bath particles.

At equilibrium the bath particle concentration is uniform and the net osmotic force is zero. However, if there is a nonuniform concentration of bath particles, either caused by an externally imposed concentration gradient or by the motor itself via a chemical reaction on its surface, there will be a net osmotic force on the motor. This force must be balanced by an externally imposed force (via, e.g., optical

tweezers) to hold the motor fixed, or by the hydrodynamic Stokes drag force from the solvent $F^{hyd} = -6\pi\eta aU$, where η is the viscosity of the solvent and U is the motor velocity. (A formal statistical mechanical derivation follows the work on single particle motion in colloidal dispersions and microrheology [11,12].) An externally imposed concentration gradient gives rise to diffusiophoresis [3], whereas a surface chemical reaction alters the local concentration of bath particles and results in *autonomous* motion—namely, the osmotic motor.

Reaction-driven propulsion was discussed recently by Golestanian *et al.* [6,13]. Their propulsive mechanism is based on the thin-interfacial-limit expressions for phoretic motion [3]. Our mechanism shares the idea of a concentration gradient driving the motion but appears to be different, and is not restricted to a thin-interfacial limit, e.g., not limited to large motors. Furthermore, these authors did not discuss the conservation of mass (or volume) associated with the chemical reaction, nor did they identify the maximum velocity obtainable by a motor, two issues that are important for the motor's behavior.

To compute the osmotic force, the concentration distribution of bath particles about the motor is needed. The bath particles are divided into reactants, labeled R, and products P. On the reactive portion of the motor surface: $R \rightarrow sP$, where for each reactant particle 's' product particles are produced; s can take any value greater than or equal to zero. Conservation of mass requires that $m_R = sm_P$, where m_R is the mass of the reactant particle and m_P that of the products. For spherical particles of the same density conservation of mass is equivalent to conservation of volume and therefore $b_R = s^{1/3}b_P$, where b_R and b_P are the radii of the reactants and products, respectively. The rate of consumption of R on the reactive surface is r_R, and the production of P is $r_P = -sr_R$.

We first consider a fixed motor. Since the reaction only takes place at the motor surface, the reactants and products diffuse in the surrounding fluid with translational diffusivities D_R and D_P, respectively, and their concentrations satisfy Laplace's equation. For the reactant: $\nabla^2 n_R = 0$, subject to the imposed concentration far from the motor, n_R^∞, and the flux to the motor is balanced by the reaction on the motor surface: $n \cdot \nabla n_R = r_R(a + b_R)/D_R$. All lengths have been nondimensionalized by the sum of the motor and reactant radii: $a + b_R$. The products satisfy a similar equation with the subscript R replaced by P. However, the osmotic force is proportional to the *total* concentration of bath particles $n_b = n_R + n_P$, which satisfies $\nabla^2 n_b = 0$, subject to $n_b^\infty = n_R^\infty + n_P^\infty$, and at the motor surface $n \cdot \nabla n_b = r_R(a + b_R)/D_R \times (1 - sD_R/D_P)$. Defining the scaled concentration differences: $\bar{n}_R' = (n_R - n_R^\infty)/n_R^\infty$ and $\bar{n}_b' = (n_b - n_b^\infty)/n_R^\infty(1 - sD_R/D_P)$ it is easy to see that $\bar{n}_R'$ and $\bar{n}_b'$ satisfy the same Laplace equation and boundary conditions. Thus, only the reactant concentration profile is needed to completely solve the problem for all

stoichiometries and diffusivity ratios. The osmotic force is

$$F^{osm} = -n_R^\infty kT(a + b_R)^2\left(1 - s\frac{D_R}{D_P}\right)\int_{r=1} n\bar{n}_b'(\mathbf{x})d\Omega,$$

(1)

where $d\Omega = dS/(a + b_R)^2$ is the solid angle [14].

The stoichiometry/diffusivity factor, $(1 - sD_R/D_P)$, tells how many products are produced per reactant, s, and how fast the products diffusive relative to the reactants, D_R/D_P. And it is this combination that governs the behavior. If we had simply $R \rightarrow P$ (or $s = 1$) and the product had the same diffusivity as the reactant, the net osmotic force would be identically zero as it must be. However, if the reactants and products have different diffusivities, say because the reaction changes the "shape" of the particle, or perhaps its interactions with the solvent (hydrophillic or hydrophobic), then even if only one product is produced for each reactant there will still be a net osmotic force on the motor. The *sign* of the force will depend on which diffuses faster. And similar arguments apply for $s \neq 1$.

As a first analysis consider a first-order reaction with rate constant κ (units of velocity), i.e. $r_R = \kappa n_R$. The reactant concentration profile is governed by the ratio of the speed of reaction to that of diffusion—the Damköhler number $Da = \kappa(a + b)/D$. We have dropped the subscript R for the reactant and will simply refer to the reactant as a bath particle. The boundary condition at the motor surface now becomes $n \cdot \nabla \bar{n}' = Da(\bar{n}' + 1)h(n)$. The distribution of reaction on the surface is determined by the dimensionless function $h(n)$, which we take to be 1 on the reactive half and 0 on the passive half. Since the detailed stoichiometry/diffusivity appears as a scale factor in the net osmotic force (1), we discuss below the case when
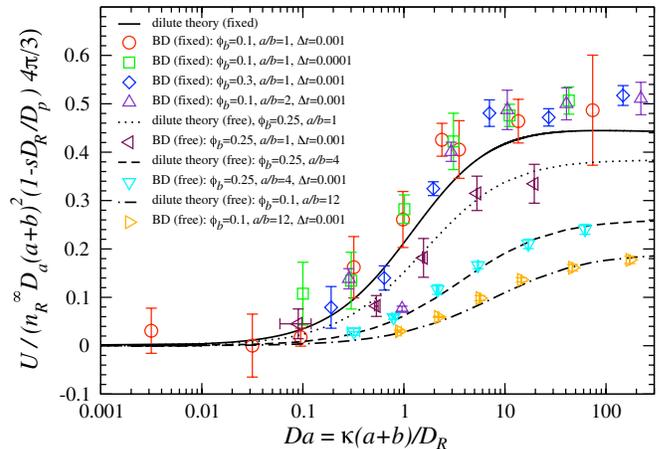

FIG. 1 (color online). The scaled osmotic velocity for a motor with a first-order reaction on half of its surface plotted against Da for various values of $\phi_b(1 + a/b)^2$. Here, $D_a = kT/6\pi\eta a$ is the Stokes-Einstein-Sutherland "diffusivity" of the motor [cf. Eq. (2)]. The theoretical predictions (curves) are compared with BD simulations (symbols). The solid curve corresponds to the fixed motor shown for comparison.

$sD_R/D_P \rightarrow 0$, which would occur if the products are much more diffusive than the reactants or when the reactant is consumed ($s = 0$) by the motor [15].

The concentration distribution of bath particles can be found analytically by separation of variables, and Fig. 1 shows the nondimensional osmotic force (expressed as a Stokes velocity) as a function of Da. The open symbols in the figure are the results of conventional hard-sphere Brownian dynamics (BD) simulations [16,17], modified to allow for surface reaction. As the theory predicts, the scaled osmotic force is independent of the size ratio of motor to bath particles, a/b, the bulk concentration of the bath particles expressed as their volume fraction, $\phi_b = n_b^\infty b^3 4\pi/3$, and from the time step Δt used in the simulations. Bath particles are consumed on the reactive side decreasing their local concentration near the motor. Thus, there are more collisions with bath particles on the passive side, resulting in an imbalanced osmotic pressure and a force on the motor in the direction of the decreasing bath particle concentration. For slow reactions, the osmotic force is linear in Da: $F^{\mathrm{osm}} \sim n_R^\infty kT(a + b)^2(1 - sD_R/D_P)\mathrm{Da} = n_R^\infty(a + b)^3(1 - sD_R/D_P)6\pi\eta b\kappa$, where we have used the Stokes-Einstein-Sutherland expression for the bath particle diffusivity $D = kT/6\pi\eta b$. This has a simple physical interpretation: each bath particle reacting with the motor strikes the motor with speed κ and thus hydrodynamic force $6\pi\eta b\kappa$ and there are $n_R^\infty(a + b)^3$ colliding bath particles. The stoichiometry/diffusivity factor, $(1 - sD_R/D_P)$, then giving the net osmotic force. At the other extreme of high Da, or fast reaction, the concentration on the reactive half is zero as the reaction is now diffusion limited. The osmotic force saturates and simply scales as the jump in concentration from the passive ($n_R \approx n_R^\infty$) to reactive ($n_R = 0$) side times the area: $F^{\mathrm{osm}} \sim n_R^\infty kT(a + b)^2(1 - sD_R/D_P)$. The transition from reaction to diffusion controlled occurs, appropriately, at a Damköhler number of unity.

It is instructive to ask what is the magnitude of the force that must be exerted on the motor to keep it fixed? The maximum force occurs in the large Damköhler number limit for large motors ($a \gg b$). For a motor of $a = 1$ μm with a 0.1 M bath particle concentration, the osmotic force is of order 0.2 μN, an easily measurable force. In fact, it is rather large as optical tweezers typically exert nano-Newton forces and biological motors exert pico-Newton forces. Indeed, if the motor were released it would travel with a speed of order 10 m/s. This surprising and aphysical result is resolved by noting that the motor cannot travel any faster than the bath particles can diffuse—that is, no faster than their diffusive velocity $v_{\mathrm{bath}} \sim D/(a + b)$. If the motor were to move faster than this velocity, the bath particles could not keep up, and the motor would loose the propulsive force that caused it to move in the first place.

The resolution of this paradox is to recognize that, in a frame of reference traveling with the free motor, there will

be an advective flux of bath particles towards the motor that will alter the concentration distribution about the motor and consequently, the propulsive osmotic force. The strength of the advective flux compared to the diffusive motion is given by a Péclet number $\mathrm{Pe} = U(a + b)/D$, where U is the as yet *unknown* free motor velocity. And now there will be Péclet numbers for both the reactants, $\mathrm{Pe}_R = U(a + b_R)/D_R$, and products, $\mathrm{Pe}_P = U(a + b_P)/D_P$, and they differ by the diffusivity ratio. The scaled reactant concentration distribution now satisfies the advection-diffusion equation $\nabla^2 \bar{n}_R' = -\mathrm{Pe}_R \partial \bar{n}_R'/\partial z$, where the direction of motion is taken to be the z direction. The products also satisfy the same equation with R replaced by P. The *total* concentration $\bar{n}_b'$ does not satisfy the same equation as the reactants, unless $\mathrm{Pe}_R = \mathrm{Pe}_P$, which will be true in the small and large Péclet number limits. The osmotic force is still scaled as before, however, and the unknown velocity is found from balancing the Stokes drag on the motor with the osmotic force:

$$U = -\frac{kT}{6\pi\eta a} n_R^\infty(a + b)^2 \left(1 - s\frac{D_R}{D_P}\right)\int \boldsymbol{n}\,\bar{n}_b'(\boldsymbol{x})d\Omega, \quad (2)$$

where the total concentration $\bar{n}_b'(\boldsymbol{x})$ now depends on the Damköhler and Péclet numbers. Note that the motor velocity, and thus the Péclet numbers, are unknown and must be determined self-consistently along with the coupled concentration distributions $\bar{n}_b'$ and $\bar{n}_R'$ from the advection-diffusion equations. This is somewhat involved, and here we discuss the limiting case of $sD_R/D_P \rightarrow 0$ for which the product distribution drops out and the bath particle concentration is the same as that of the reactants.

Figure 1 shows the predictions for the free motor velocity as a function of Da from the analytical solution. In contrast to the fixed motor case (the solid line), the speed of
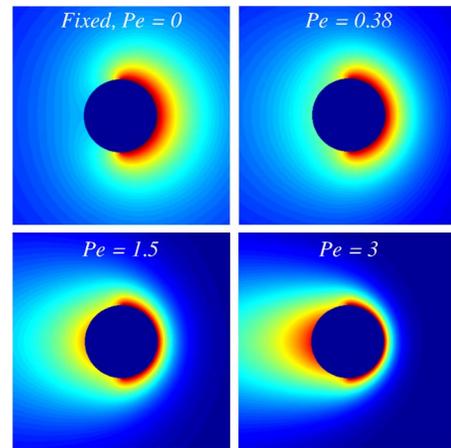

FIG. 2 (color online). Density profiles in the symmetry plane of the osmotic motor at Da = 100. The four panels correspond to the four curves (from top to bottom) in Fig. 1. Red is low bath particle concentration and blue the uniform level far from the motor. The right half of the motor is reactive and its motion is from left to right.

the motor now *does* depend on a/b and on ϕ_b (even though the bath particles form an ideal gas). As before, the open symbols correspond to BD simulations for the same conditions of volume fraction and size ratio as in the theory and show excellent agreement. The curves correspond to increasing the product $\phi_b(1 + a/b)^2$, which follows directly from (2) and corresponds to the number of bath particles within a bath particle radius of the motor surface.

Figure 2 shows density plots of the bath particle concentration near the motor at Da = 100, but for different values of $\phi_b(1 + a/b)^2$, corresponding to each of the four curves in Fig. 1. Also shown on the plots are the resulting Péclet numbers corresponding to the motor velocities. As the Péclet number increases the advection of the bath particles past the motor distorts the bath particle concentration, shrinking the bath-particle-depleted region in front of the motor and leaving a trailing "wake" of reduced bath particle concentration. At even modest motor velocities (modest Pe) most of the rear of the motor has a very low bath particle concentration, which reduces the osmotic force and thus limits the speed of the motor. This self-regulation results in a maximum motor velocity of order the diffusion velocity of the bath particles $U_{max} \sim v_{bath} \sim D/(a + b)$. For a 1 μm sized motor and nanometer-sized bath particles the maximum motor velocity is now of order 10 μm/s, a much more reasonable velocity, and one that is in fair agreement with the motivating experiments of Paxton *et al.* [4].

The results in Fig. 1 show that the fixed motor is the limit as $\phi_b(1 + a/b)^2 \to 0$ (Pe = 0) of the free motor, corresponding to an infinitely dilute suspension of bath particles. This is as it should be, because whether the motor is fixed or free is just a change of reference frame. For a fixed motor there will be an advective flux at infinity to supply reactive bath particles to the motor. This also implies that the motor will induce a fluid flow to supply the bath particles and can be used as a pump—a novel microfluidic pump (and mixer).

In this analysis we neglected rotary Brownian motion [18] and hydrodynamic interactions between particles. Hydrodynamics would quantitatively (not qualitatively) affect the motor speed and can be included via the well-known low-Reynolds number hydrodynamic mobility expressions [10] for the bath particle diffusivity and the advective velocity. Also, the entropic Brownian force on the motor contains an additional term that is the integral of the spatial variation of the relative hydrodynamic mobility (see [12] for the analogous microrheology problem).

Clearly, neither the motor nor the bath particles need be spherical, nor must the bath particles form an ideal gas. And a variety of behaviors is possible depending on the nature of the chemical reaction at the motor surface, the number of motors present, etc. Rotary motion is also

possible by having reactive patches strategically located about the motor surface [19].

Osmotic propulsion provides a simple means to convert chemical energy into mechanical motion and work, and can impact the design and operation of nanodevices, with applications in directed self-assembly of materials, thermal management of micro- and nanoprocessors, and the operation of chemical and biological sensors. Studies of autonomous motors may also help to understand chemo-mechanical transduction observed in biological systems [20] and to create novel artificial motors that mimic living organisms and which can be harnessed to perform desired tasks.

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