REACTION-INDUCED MOTION: CHEMICAL SWIMMING, SAILING AND SURFING

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Summary Catalytic nanomotors convert chemical energy into motion by generating concentration gradients in reactant and product species whose subsequent diffusion entrains the motor, a process we call 'chemical swimming.' Motion can also be realized by controlling the shape, as opposed to reactivity, of the motor leading to 'chemical sailing.' Finally, motors confined to an interface can 'surf' the reaction-induced concentration gradient.

INTRODUCTION

The design of nanoengines that can convert stored chemical energy into motion is a key challenge of nanotechnology, especially for engines that can operate autonomously. Recent experiments have demonstrated that it is possible to power the motion of nanoscale and microscale objects by using surface catalytic reactions – so-called catalytic nanomotors [1]. The precise mechanism(s) responsible for this motion is(are) still debated, although a number of ideas have been put forth [2, 3, 4]. Here, a very simple mechanism is discussed: A surface chemical reaction creates local concentration gradients of the reactant (the fuel) and product species. As these species diffuse in an attempt to re-establish equilibrium, they entrain the motor causing it to move. This process can be viewed either as osmotic propulsion or as self-diffusiophoresis – or more figuratively as 'chemical swimming.' The concentration distributions are governed by the ratio of the surface reaction velocity to the diffusion velocity of the reactants and/or products. For slow reactions the reaction velocity determines the self-propulsion. When surface reaction dominates over diffusion the motor velocity cannot exceed the diffusive speed of the reactants. The implications of these features for different reactant concentrations and motor sizes are discussed and the theoretical predictions are compared with Brownian Dynamics simulations. We also show that it is possible to obtain directed reaction-induced motion by controlling the *shape* of the motor – 'chemical sailing' – which may lead to easier fabrication of nanomotors. Finally, when motors are confined to an interface they can 'surf' the reaction-induced concentration gradient. Through these mechanisms the motor is able to harness the ever present random thermal motion via a chemical reaction to achieve directed autonomous motion.

BASIC MECHANISM

The catalytic nanomotor and the reactive chemical species are modeled as colloidal particles dispersed in a continuum solvent, whose dynamics are governed by the Smoluchowski equation [4]: $\partial P_N/\partial t + \sum_{\alpha=1}^{N} \nabla_\alpha \cdot \boldsymbol{j}_\alpha = 0$, with the αth particle flux $\boldsymbol{j}_\alpha = -\boldsymbol{D}_{\alpha\beta} \cdot \nabla_\beta [V/k_BT + \ln P_N] P_N$. Here, $P_N(\{\boldsymbol{x}\}, t)$ is the N-particle probability density function for finding the particles in a given configuration $\{\boldsymbol{x}\}$ at time t, ∇_α is the gradient operator with respect to the coordinates of the αth particle, V is the interparticle potential, k_BT is the thermal energy, and the diffusivity $\boldsymbol{D}_{\alpha\beta} = k_BT\boldsymbol{M}_{\alpha\beta}$, where the hydrodynamic mobility $\boldsymbol{M}_{\alpha\beta}$ gives the velocity of particle α due to a force exerted on particle β. At equilibrium the Boltzmann distribution holds $P_N^{eq} \sim \exp(-V/k_BT)$ and both the force on and flux of each individual particle is zero.

The interest is in the motion of the nanomotor, which we denote as particle '1'; particles 2 through N are reactive 'bath' particles. Integrating the Smoluchowski over the coordinates of the $N-1$ bath particles and taking the Fourier transform with respect to $\boldsymbol{x}_1$, with wavevector $\boldsymbol{k}$ and denoted by $\hat{}$, the probability density for finding the catalytic nanomotor, $\hat{P}_1(\boldsymbol{k}, t)$, satisfies

$$\frac{\partial \hat{P}_1}{\partial t} + i\boldsymbol{k} \cdot \langle \boldsymbol{U}_1 \rangle_1 \hat{P}_1 + \boldsymbol{k}\boldsymbol{k} : \langle \boldsymbol{D}_{11} \rangle_1 \hat{P}_1 = 0, \tag{1}$$

where $\langle \boldsymbol{U}_1 \rangle_1$ is the advective velocity of particle 1, the nanomotor, averaged over the positions of all the reactive particles, and $\langle \boldsymbol{D}_{11} \rangle_1$ is its diffusivity. Our interest here is in the net advective motion only; the effective diffusivity will not be discussed further. For constant $\langle \boldsymbol{U}_1 \rangle_1$ and $\langle \boldsymbol{D}_{11} \rangle_1$, $\hat{P}_1$ has the form expected for advection and diffusion of a Brownian particle $\hat{P}_1 \sim \exp(-i\boldsymbol{k} \cdot \langle \boldsymbol{U}_1 \rangle_1 t - \boldsymbol{k}\boldsymbol{k} : \langle \boldsymbol{D}_{11} \rangle_1 t)$.

The advective flux, $\langle \boldsymbol{U}_1 \rangle_1 \hat{P}_1$, depends on the microstructure – the distribution of reactant/product particles about the nanomotor. For dilute reactants, only the two-particle distribution function is needed: $\hat{P}_2(\boldsymbol{k}, \boldsymbol{r}, t)$, where $\boldsymbol{r} = \boldsymbol{x}_2 - \boldsymbol{x}_1$ is the relative position of bath and catalytic particles. A similar distribution function is written for the product particles. Here we take the chemical reaction at the nanomotor surface to be an irreversible reaction in which s products are produced upon reaction: $R \to s\,P$. What is important is not only the stoichometry of the reaction, s, but also how fast the reactants diffuse relative to the products D_R/D_P. It was shown in [3] that what is important is the stoichometry/diffusivity factor $(1 - sD_R/D_P)$ and that the joint probability including both reactants and products can be written as $\hat{P}_2(\boldsymbol{k}, \boldsymbol{r}, t) = n_R^0(1 - sD_R/D_P) g^{eq}(\boldsymbol{r}) \hat{f}(\boldsymbol{k}, \boldsymbol{r}, t) \hat{P}_1(\boldsymbol{k}, t)$, where n_R^0 is the constant number density of reactant particles far from the catalytic particle, and $g^{eq}(\boldsymbol{r})$ is the equilibrium pair-distribution function, i.e. the probability for finding a reactant/product

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particle at position $\boldsymbol{r}$ relative to the catalytic nanomotor. Straightforward working shows [4] that the average advective velocity of the catalytic nanomotor is given by

$$\langle \boldsymbol{U}_1 \rangle_1 = n_R^0 k_B T \, (1 - sD_R/D_P) \int (\boldsymbol{M}_{11} - \boldsymbol{M}_{12}) g^{eq} \cdot \nabla_r f_0 \, d\boldsymbol{r}, \tag{2}$$

where $\hat{f}(\boldsymbol{k}, \boldsymbol{r}, t) \sim f_0(\boldsymbol{r}, t) + O(k)$ for small k.

Equation (2) shows clearly that there will be net advective motion of the catalytic nanomotor when the departure of the reactant concentration from equilibrium – f_0 – has a dipolar character, as is the case for spherical catalytic nanomotors with an asymmetric reactivity on their surfaces [1]. This was the starting point for the osmotic motor analysis in [3]. (Note that $n_R^0 k_B T f_0 = n_R(\boldsymbol{r}) k_B T$ is the local osmotic pressure of the reactants.) But (2) also shows that even with a uniform reactivity – a spherically symmetric f_0 – net motion can result if the interparticle potential – $g^{eq} \sim \exp(-V(\boldsymbol{r})/kT)$ – has a dipolar character, or if the hydrodynamic mobility of the catalytic nanomotor, $\boldsymbol{M}_{11}$, is nonuniform over the particle surface as might occur for a Janus particle with a portion of its surface modified to slip. Indeed, (2) applies equally well to nonspherical particles and can give rise to 'shaped'-induced motion even for uniform reactivity. (For nonspherical nanomotors, as well as spherical motors with an asymmetric surface reactivity, we consider the motor's orientation to be fixed.)

The departure of the reactant/product distribution from equilibrium, f_0, is governed by the reaction-advection-diffusion equation obtained from the pair-Smoluchowski equation and can be found in [4]. For a first order irreversible reaction with rate constant κ, the nonequilibrium distribution is governed by the ratio of the rate of reaction κ to diffusion D_R/a, known as the Damköhler number $Da = \kappa a/D_R$, where a is the size of the motor.

RESULTS

The speed of the motor varies between two limits: At small Da where diffusion dominates, the motor speed is proportional to κ. At large Da where the reaction is diffusion limited, the speed is limited by the diffusion velocity of the reactants D_R/a. These fundamental behaviors are illustrated in figure 1 (left) where the nondimensional motor velocity is shown as a function of the Damköhler number for various concentrations of reactants ($\phi_b = 4\pi n_R^0 b^3/3$) and motor sizes ($a/b$) for a half reactive nanomotor. (Here, b is the size of a reactant particle.) The right panel shows the corresponding reactant concentration profiles at $Da = 100$ and the corresponding determined Peclet numbers $Pe = |\langle U_1 \rangle_1| a/D_R$ (from [3]).

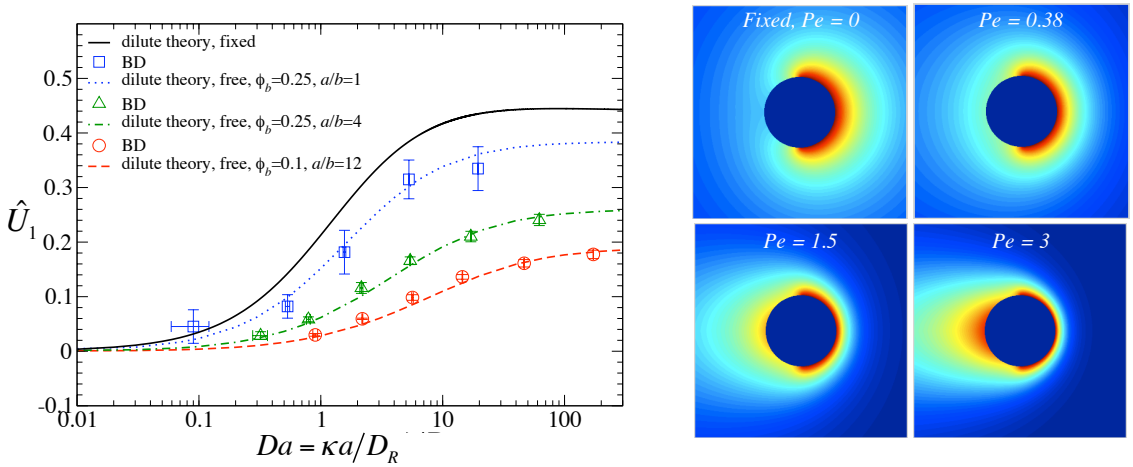

Figure 1. The nondimensional catalytic nanomotor velocity as a function of Da for various reactant concentrations (ϕ_b) and motor sizes (a/b). The right panel shows the corresponding reactant concentration distribution about the motor at $Da = 100$. The motor velocity has been scaled as $\hat{U}_1 = \langle U_1 \rangle_1 / [(n_R^0 k_B T a^2/6\pi\eta a) 4\pi (1 - sD_R/D_P) L(1)/3]$, where $L(1)$ is a non dimensional hydrodynamic function (see [4]).

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