Self-propelled Microswimmer Actuated by Stimuli-sensitive Bilayered Hydrogel

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Supporting Information

Computational Methodology

In order to model the hydrodynamics of a microswimmer made of a responsive polymeric gel in a viscous solvent, we used dissipative particle dynamics (DPD).[1-3] DPD is a mesoscale, coarse-grained approach in which clusters of molecules are represented by beads that interact *via* "soft" pair-wise potentials. The soft interacting potential makes simulating polymeric systems, in which processes are characterized by relatively large time and space scales, possible. Furthermore, the pair-wise potentials locally conserve linear and angular momentum and therefore allow for accurate hydrodynamic simulations.

In DPD, bead dynamics is governed by three interactions: conservative forces $\mathbf{F}_{ij}^{C}$, dissipative forces $\mathbf{F}_{ij}^{D}$, and stochastic (or random) forces $\mathbf{F}_{ij}^{R}$. The total force acting on a single DPD bead i is a sum of these forces over j neighboring beads within a cutoff radius r_C. The conservative force, $\mathbf{F}_{ij}^{C} = a_{ij}\omega(r_{ij})\hat{\mathbf{r}}_{ij}$, accounts for compressibility. Here, a_{ij} sets the "soft" repulsion between any two given beads (i and j) and $\omega(r_{ij}) = 1 - \hat{r}_{ij}$ is the weighting function. Moreover, $\hat{r}_{ij} = r_{ij}/r_C$, $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|$ is the separation distance between interacting beads, and $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/r_{ij}$. The combination of dissipative and random forces defines a thermostat that keeps the system in thermal equilibrium. The dissipative force is given by $\mathbf{F}_{ij}^{D} = -\gamma\omega^2(r_{ij})(\hat{\mathbf{r}}_{ij} \cdot \mathbf{v}_{ij})\hat{\mathbf{r}}_{ij}$ which introduces viscosity, while the stochastic force $\mathbf{F}_{ij}^{R} = \sigma\omega(r_{ij})\xi_{ij}(\Delta t)^{-1/2}\hat{\mathbf{r}}_{ij}$ accounts for random thermal fluctuations.[1] The factors γ and $\sigma = \sqrt{2k_B\bar{T}\gamma}$ characterize the strength of the respective forces, and $\mathbf{v}_{ij} = \mathbf{v}_i - \mathbf{v}_j$ is the relative velocity of bead i with respect to bead j. Furthermore, k_B is the Boltzmann constant, $\bar{T}$ is the temperature, and ξ_{ij} is a standard normal random variable with zero mean. In our simulations, we used a time step of $\Delta t = 0.01$ and set other parameters to $\gamma = 4.5$, $a_{ij} = 25$, $k_B\bar{T} = 1$, $m = 1$, $\rho = 3$, and $r_C = 1$, all in DPD units. These parameters effectively simulate a solvent with shear viscosity $\mu = 0.849$. Our simulations were carried out in an $80 \times 80 \times 80$ periodic cubic domain.

The responsive gel polymer network is modeled as a random network of interconnected elastic filaments.[4, 5] We generate this polymer network in three steps. First, we randomly distribute seed DPD beads with number density $n_s = 0.5$ within a $(d_R + d_P)\times L \times L$ box at the center of the computational domain. Next, we connect closest seed beads with elastic filaments with an average connectivity of 8. Then we remove triangular portions out of the sides of the rectangular network to form the X-shaped geometry of the swimmer. In our simulations, we keep constant $L = 40$ and $d_R = 4$, whereas d_P is varied to alter swimmer thickness.

The elastic filaments forming the gel network consists of DPD beads chained by harmonic bending and stretching springs. The stretching spring potential is given by $U_s = \frac{k_s}{2}\left(r - r_{eq}\right)$, where $r_{eq} = 0.3$ is the equilibrium length and $k_s = 30$ is the spring constant. The bending rigidity for the polymer network is governed by the bending potential, $U_b = k_b\left(1+\cos\theta\right)$, where θ is the angle between two interacting beads and $k_b = 50$ is the bending stiffness. The swelling response of the bifaced hydrogel swimmer is modeled by instantaneously increasing both the equilibrium length r_{eq} and the repulsion a_{ij} between beads forming the responsive gel layer to yield a desired value of the gel swelling ratio ε. When the stimulus is removed, the altered r_{eq} and a_{ij} are restored to their initial values. We have recently showed that this model allows us effectively to simulate the kinetics of volume transition in responsive gels.[5]

Scaling Analysis of Bilayered Hydrogel Swimmer

We use scaling analysis to estimate the bending and stretching time scales, t_b and t_e, that define swimmer kinetics. The time of stretching can be evaluated by balancing elastic forces due to gel swelling and the viscous forces imposed by the solvent. To this end, we first evaluate the magnitude of stretching induced by the swelling of the responsive layer. The elastic force on each layer can be estimated as $F_e \sim EA\Delta s/L$, where $\Delta s = s_{\max} - L$ and $\Delta s = L\varepsilon^{1/3} - s_{\max}$ for the passive and responsive layers, respectively. Here, $s_{\max}$ is the swimmer size in the swollen state, in which case the elastic forces in the passive and responsive layers are equal, i.e. $F_{eP} = F_{eR}$. From this force balance we find that $s_{\max}/L \sim \left(\varepsilon^{1/3} + R\right)/\left(1+R\right)$. This scaling suggests that when R increases, the swollen length ratio decreases and approaches unity, meaning that the swimmer with large R is unable to expand due to larger resistance of the passive layer. On the other hand, when R approaches zero, $s_{\max} \sim L\varepsilon^{1/3}$, which is the swollen length of the responsive layer without the presence of the passive layer. Note that s_{max} does not depend explicitly on Young's modulus E in this linear scaling argument. The viscous force on the swimmer during extension is $F_v \sim C_e \mu U_e L$, where the extensional velocity is $U_e \sim \Delta s / t_e$ and C_e is the drag coefficient due to the fluid flow along the extending swimmer. Thus, balancing elastic and viscous forces yields an estimate for the swimmer expansion time $t_e \sim C_e \mu L^2 / EA$.

The combination of compressive and extensional forces in the bilayered swimmer creates an internal moment that induces swimmer bending. This internal moment can be estimated as $M_b \sim 0.5 F_e \left(\varepsilon^{1/3} d_R + d_P\right)$. Because bending moment is proportional to curvature, $M_b = \kappa_{\max} EI$, where EI is the bending rigidity, we estimate the maximum curvature as $\kappa_{\max} L \sim \dfrac{6R\left(1-\varepsilon^{-1/3}\right)}{\varepsilon^{1/3}\left(1+R\varepsilon^{-1/3}\right)^3}\left(\dfrac{L}{d_R}\right)$. This scaling shows that the curvature depends on the aspect ratio L/d_R, thickness ratio R, and swollen length ratio $\varepsilon^{1/3}$. Just like the swollen swimmer size, the curvature does not explicitly depend on E. When R is either large or small, the curvature approaches zero indicating that the swimmer does not bend. Indeed, for small R, the thin passive layer is unable to resist the expansion, generating a weak internal bending moment. For large R, the thick passive layer with large EI suppresses the bending of the swimmer. The scaling indicates an optimum value of $R = 0.5\varepsilon^{1/3}$ that maximizes the swimmer curvature.

Similar to the extensional time scaling, we can determine the time scale for bending by balancing the moments due to the elastic force and the viscous drag force on the moving swimmer arm given by $M_v \sim C_b \mu U_b L^2 / 4$. Here, the bending velocity $U_b \sim \kappa_{\max} L^2 / 8 t_b$ is estimated as the velocity of the arm tips, and C_b is the drag coefficient associated with swimmer bending. By equating the internal moments due to elastic and viscous forces, we estimate the swimmer bending time as $t_b \sim C_b \mu L^4 / 32EI$. Thus, the ratio of the extensional and bending time scales is $\dfrac{t_e}{t_b} \sim \dfrac{C_e}{C_b}\dfrac{8\left(1+R\varepsilon^{-1/3}\right)^3}{3R\varepsilon^{-1/3}}\left(\dfrac{d_R}{L}\right)^2$. The scaling shows that the time ratio depends on the ratio of the drag coefficients $C_e/C_b \sim 0.5$,[6] the swimmer aspect ratio d_R/L that is defined by the swimmer geometry, and $R\varepsilon^{-1/3}$, the thickness ratio of the swollen swimmer. There is no dependence on material properties other than the swelling ratio ε.

A difference between time scales associated with swimmer bending and extension leads to time irreversible motion. Thus, t_e/t_b should be relatively small to generate swimmer unidirectional motion in a viscous fluid. To obtain this condition the aspect ratio d_R/L should be small and the swollen thickness ratio $R\varepsilon^{-1/3}$ should be about 0.5.

References

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