

Electrolytes and electrokinetics

Many fluids relevant to microfluidics contain dissolved ionic species and / or suspended particles with net electronic charges.

Both the fluids and these particles can therefore be manipulated by electric fields.

We will look at:

- Screening in electrolytes
- Interfaces and potential profiles
- Electrophoresis
- Dielectrophoresis

Electrolytes

Typical composition of an electrolyte:

- Buffer solution, containing equal amounts of positive and negatively charged ionic species - overall neutral.
- Charged particles in suspension - usually much less charge from these than either the total positive or negative charge density from the ionic species.

Charge density: $\rho_e = \sum_i z_i e n_i$

z_i = charge of species i (e.g. +2, -1, etc.)

n_i = concentration of species i (number per volume).

We know the charge density must obey the Poisson equation....

Debye length

In equilibrium,

$$\nabla^2 \phi = 0 \quad \text{in bulk of solution (neutral!)}$$

$$\nabla^2 \phi = -\frac{\rho_e}{\kappa \epsilon_0} \quad \text{in general.}$$

Assume $\phi_0(\mathbf{r})$ = equilibrium electrostatic potential. Then for perturbation away from equilibrium at finite temperature:

$$\hat{\phi} \equiv \phi - \phi_0$$

$$\rho_e = \sum_i z_i e n_{i0} \exp\left(-\frac{z_i e \hat{\phi}}{k_B T}\right)$$

This is just a Boltzmann factor from statistical mechanics;
Thermal energy allows excursions from equilibrium.

Debye length

$$\nabla^2 \hat{\phi} = -\frac{1}{\kappa \epsilon_0} \sum_i z_i e n_{i0} \exp\left(-\frac{z_i e \hat{\phi}}{k_B T}\right)$$

Expand for small perturbations / high temperatures:

$$\nabla^2 \hat{\phi} \approx -\frac{1}{\kappa \epsilon_0} \sum_i z_i e n_{i0} + \frac{e^2}{\kappa \epsilon_0 k_B T} \sum_i z_i^2 n_{i0} \hat{\phi}$$

~ 0 for equilibrium neutrality

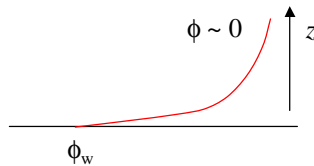
$$\nabla^2 \hat{\phi} \approx \frac{e^2}{\kappa \epsilon_0 k_B T} \sum_i z_i^2 n_{i0} \hat{\phi} \equiv \frac{1}{\lambda_D^2} \hat{\phi}$$

$$\lambda_D \equiv \left(\frac{e^2}{\kappa \epsilon_0 k_B T} \sum_i z_i^2 n_{i0} \right)^{-1/2}$$

Debye length - particular case

$$\nabla^2 \hat{\phi} = -\frac{1}{\kappa \epsilon_0} \sum_i z_i e n_{i0} \exp\left(-\frac{z_i e \hat{\phi}}{k_B T}\right)$$

A particular case that often comes up is for a symmetric electrolyte (e.g. Na⁺, Cl⁻), a 1d problem:



$$\frac{d^2 \hat{\phi}}{dz^2} \approx \frac{2ezn_0}{\kappa \epsilon_0} \sinh\left(\frac{ze\hat{\phi}}{k_B T}\right) \quad \text{Poisson-Boltzmann equation}$$

Debye length

$$\nabla^2 \hat{\phi} \approx \frac{1}{\lambda_D^2} \hat{\phi} \quad \lambda_D \equiv \left(\frac{e^2}{\kappa \epsilon_0 k_B T} \sum_i z_i^2 n_{i0} \right)^{-1/2}$$

For (1d) case of wall at a potential ϕ_w with respect to the bulk solution, the solution is of the form

$$\hat{\phi} = \phi_w \exp\left(-\frac{z}{\lambda_D}\right)$$

That is, the ions in the solution screen the potential of the wall over a length scale given by the Debye length.

Trends:

- Better screening for higher concentrations of ions
- Worse screening for higher temperatures

Note: κ for the solution can be large and frequency dependent!

Debye length - numbers

$$\lambda_D \equiv \left(\frac{e^2}{\kappa \epsilon_0 k_B T} \sum_i z_i^2 n_{i0} \right)^{-1/2}$$

So, the potential from walls (or small charged objects) is almost completely screened over a distance $\sim 3 \lambda_D$.

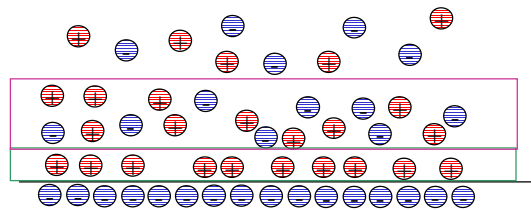
In pure water (pH = 7), screening just from H^+ and OH^- in equilibrium. At room temperature, $\lambda_D \sim 1$ micron.

In 1 M KCl in water, $\lambda_D \sim 0.3$ nm.

Remember, κ for water at low frequencies is ~ 80 .

Note: for big microfluidic devices, these charge effects only matter near interfaces, but for nanoscale fluidic systems with low ionic concentrations, one must worry about poor screening.

Debye screening physics



Stern layer - ions opposite in charge to surface charge of wall material; effectively immobilized due to strong interactions with wall.

Gouy-Chapman layer - diffuse ions, net same sign as Stern layer, but mobile.

Together, these are called the electric *double layer*.

Debye screening occurs in the diffusive layer.

The potential at the edge of the Stern layer is called the *zeta* potential.

Charge density in double layer

We can quickly estimate the two-dimensional charge density bound up in the double layer:

$$\rho_e \approx -\frac{\kappa\epsilon_0}{\lambda_D^2} \hat{\phi}$$

$$\sigma_{2d,dl} = \int_0^\infty \rho_e(z) dz = -\frac{\kappa\epsilon_0}{\lambda_D} \phi_w = -\sigma_w$$

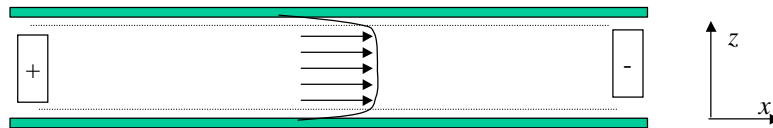
Surface charge density in double layer balances that in wall.

$$\longrightarrow \hat{\phi} \approx \frac{\sigma_w \lambda_D}{\kappa\epsilon_0} \exp\left(-\frac{z}{\lambda_D}\right)$$

The surface charge density at the wall should be a fixed property of a given material system.

Electro-osmosis

- Assume laminar flow, and channel much larger in diameter than Debye length.



- Assume steady state, no pressure gradient along channel.
- Electric field \mathbf{F} can only act on net charge, which only exists in diffusive part of double layer.
- Basic idea: charge in the diffusive double layer is accelerated by electric field, and has no-slip boundary condition at the walls. Viscosity dictates a uniform velocity profile across the middle of the channel.

Electro-osmosis

Best approach to finding $u(z)$ is to solve Navier-Stokes for this case:

$$\rho_m \frac{Du}{Dt} = 0 = -\cancel{\nabla p} + \eta \nabla^2 u + \rho_e F$$

↑ steady state.
 ↓ 0

Note: have omitted gravity and used incompressible form.

Knowing the charge density, for fully developed flow

$$\eta \frac{\partial^2 u}{\partial z^2} = \frac{\sigma_w F}{\lambda_D} \exp\left(-\frac{z}{\lambda_D}\right)$$

Using no-slip at the wall, near the bottom wall

$$u(z) \approx \frac{\sigma_w F \lambda_D}{\eta} \left(1 - \exp\left(-\frac{z}{\lambda_D}\right)\right)$$

Electro-osmosis

Far from the double layer, $u_0 \approx \frac{\sigma_w F \lambda_D}{\eta}$

This is called “plug flow” - there’s almost no velocity gradient across the channel far from the wall, meaning almost no shear stress there.

Under certain conditions, this result may be generalized to show that the velocity field \mathbf{u}_0 and the electric field \mathbf{F} are similar:

Valid for: $\mathbf{u}_0(\mathbf{r}, t) \approx \frac{\sigma_w \lambda_D}{\eta} \mathbf{F}(\mathbf{r}, t)$

- Uniform wall surface charge density (zeta potential)
- Debye length small compared to channel geometry
- No applied pressure gradient

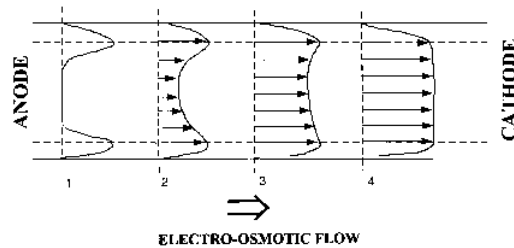
Electro-osmosis

$$\mathbf{u}_0(\mathbf{r}, t) \approx \frac{\sigma_w \lambda_D}{\eta} \mathbf{F}(\mathbf{r}, t)$$

Can define an electro-osmotic mobility: $\mu_{eo} \equiv \frac{u_0}{F}$

Note that right now it's very challenging to directly measure quantities like σ_w or equivalently the zeta potential.

Most literature values are inferred by assuming this double layer approach is correct and performing electro-osmosis measurements.



Electrophoresis

Now assume that there are small particles suspended in a background buffer solution of electrolyte.

In an applied longitudinal electric field, that buffer solution cruises along at the electro-osmotic velocity.

Further assume that the concentration of these particles is low enough that the basic double-layer physics that controls electro-osmosis still works, and that one can then worry about a double layer around each particle.

Result will be an effective surface charge on each particle due to the double layer, and a corresponding electric force that ends up being balanced by viscous drag.

Steady-state: particles move at some electrophoretic velocity relative to the electro-osmosis velocity.

Electrophoresis

That is, $q_s F = 6\pi\eta u_{ep} r_0$ ← some effective radius of particle
 ↑
 effective charge of particle

Assuming a spherical particle and given the zeta potential for the particle material, one can compute q_s :

$$q = 4\pi r_0^2 \left(-\kappa\epsilon_0 \left(\frac{\partial\phi}{\partial r} \right) \Big|_{r=r_0} \right) \approx 4\pi r_0^2 \left(\kappa\epsilon_0 \phi_\zeta \left(\frac{1}{r_0} + \frac{1}{\lambda_D} \right) \right) = 4\pi\kappa\epsilon_0 r_0 \phi_\zeta \left(1 + \frac{r_0}{\lambda_D} \right)$$

If the Debye length is big compared to the size of the particle,

$$u_{ep} = \frac{qF}{6\pi\eta r_0} = \frac{2}{3} \frac{\kappa\epsilon_0 F}{\eta}$$

Electrophoresis

If the Debye length is *small* compared to the size of the particle, the charge distribution isn't that different than the flat plate case, and we eventually get

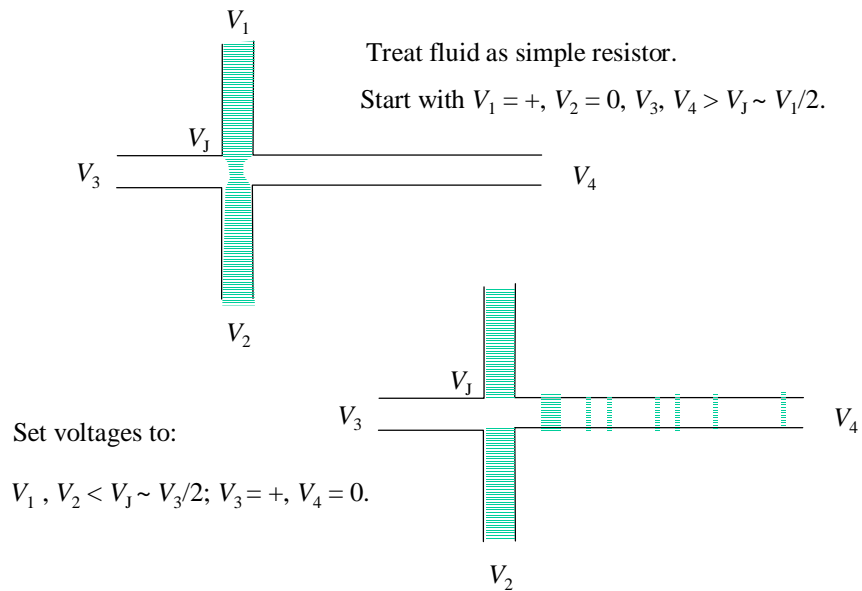
$$u_{ep} = \frac{\kappa\epsilon_0 \phi_\zeta F}{\eta}$$

Note that the two limiting cases aren't very different.

This is why electrophoresis is applicable from large sizes (cells) down to small sizes (coiled DNA) down to really small sizes (nanoparticles).

Note: the real utility here comes from the fact that ϕ_ζ depends strongly on the molecular weight and valence state of the object in question!

Microfluidic capillary electrophoresis in action



Microfluidic capillary electrophoresis

Bands get smeared by diffusion of particles within the electrolyte.

Blurring of bands after electro-osmotically traversing a distance

L of channel:

$$L_{diff} = \sqrt{D\tau} = \sqrt{D \frac{L}{u_{eo}}}$$

$$= \sqrt{D \frac{L\eta}{\sigma_w F \lambda_D}}$$

Things scale nicely for doing this in the microfluidic environment!

Biggest win: smaller L leads to shorter processing times.

Dielectrophoresis

One can also use dielectric response of particle + ionic screening cloud to move particles in an electrolyte.

Assuming some electric dipole moment $\mathbf{p}(\omega)$, and an inhomogeneous electric field, the instantaneous force on the dipole is:

$$\mathbf{f}_{dep} = \mathbf{p} \cdot \nabla \mathbf{F}$$

Of course, the effective dipole moment is frequency dependent for an ac field, because the screening cloud has some finite time response.

Generally, it is possible to have dielectrophoretic forces of *either* sign (attracted to or repelled by regions of strong electric field).

Again, microfluidic devices can use this effectively to sort small particles (ex. cells) because at small size scales it's relatively easy to get big field gradients.

Summary:

- Debye screening describes how the ions in common electrolytic fluids respond to perturbations, such as potentials due to solid interfaces.
- Double layer charge model is widely used, though microscopically measuring the parameters involved is very hard.
- Main electrokinetic effects from our point of view: electro-osmosis and electrophoresis.
- Small geometries provide many advantages for applying these phenomena.

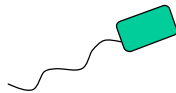
Life at Low Reynolds Number

Am. J. Phys. **45**, 2 (1977)

Very well-known paper by E.M. Purcell

Nobel Prize, 1952 for coinvention of nuclear magnetic resonance measurements

Brilliant educator - great textbook on E&M



What is the world like from the point of view of a bacterium?

That is, at a scale where viscous forces completely dominate, how do things work?

Swimming

Flagellae (with some modern info)

Efficiency and food supplies

Can we use this for our benefit?



Reynolds number and viscous forces

Reynolds number:

$$\frac{\rho v L}{\mu} \sim \frac{(\rho v^2 L^2)}{(\mu v / L)(L^2)}$$

inertial forces
viscous forces

Reynolds number $> \sim 1000-3000$ = turbulent flow

$< \sim 1000-3000$ = laminar flow

$< \sim 1$ = "creeping flow"

What is the drag force on a small spherical particle if $Re = 1$?

$$F_d = 6\pi\mu L \quad \text{Stokes' drag law}$$

$$\frac{\rho v L}{\mu} \sim 1 \rightarrow v L \sim \frac{\mu}{\rho}$$
$$\rightarrow F_d \sim (6\pi) \frac{\mu^2}{\rho}$$

Reynolds number and viscous forces

So, for a given system at $Re \sim 1$, the drag force is approximately

$$F_d \sim \frac{\mu^2}{\rho}$$

Plug in some numbers. For water, $\mu \sim 10^{-3}$ kg/ms, $\rho = 1000$ kg/m³.

Typical drag force in water is then 10^{-9} N, or 10^{-4} dynes.

Sense of scale:

Person swimming in water: $Re \sim 10^4$. To get a Re of 1 for someone ~ 2 m long in water would require swimming at a speed of 500 nm/sec (!).

Remember, the relevant length scale that determines Re is approximately the size of the object.

So, for a bacterium ~ 1 micron long swimming 30 microns/sec, $Re \sim 3 \times 10^{-5}$! Inertial forces mean nothing to the bacterium.

Length and time scales

We can get a crude estimate of how far the bacterium would drift in this situation.

Assume that the drag force on spherical bacterium.

$$F_d \sim 6\pi\mu L = -(\rho L^3) \frac{dv}{dt}$$
$$-\frac{6\pi\mu L}{\rho L^3} dt = \frac{dv}{v} \quad \longrightarrow \quad v = v_0 \exp\left(-\frac{6\pi\mu L}{\rho L^3} t\right)$$
$$x = \left[1 - \exp\left(-\frac{6\pi\mu L}{\rho L^3} t\right)\right] \frac{v_0 \rho L^3}{6\pi\mu L}$$

Timescale for these numbers: ~ 150 ns to stop.

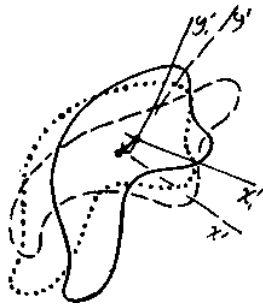
Coasting distance: $\sim 1.2 \times 10^{-3}$ nm.

—————> Conventional notion of swimming is out the window.

Swimming and reciprocal motion

Swimming = some cyclical motion intended to propel

Simplest case: deform body somehow, repeatedly.



Idea is that viscous forces act on the body at each step, and at the end of some *cycle*, the body is back in its original configuration, though translated in position.

Problem: **time-reversal symmetry**

Navier-Stokes for this case:

$$-\nabla p + \mu \nabla^2 \mathbf{u} = 0$$

Making a single motion, and then exactly reversing it (“reciprocal motion”), will put you back exactly where you started!

Scallop theorem

Making a single motion, and then exactly reversing it (“reciprocal motion”), will put you back exactly where you started!



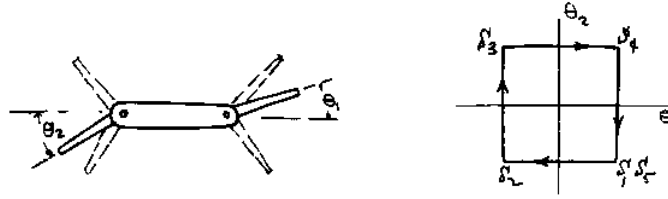
This leads Purcell to define the “Scallop theorem”.

A scallop (that is, a creature with only a single degree of freedom of motion, like one hinge) cannot swim at very low Reynolds number!

To actually make forward progress requires at least two degrees of freedom, so that one can execute a *cycle*.

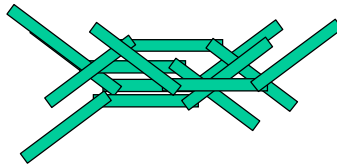
Picking which degree of freedom is *first* in the cycle is what breaks the symmetry....

Two hinges



Simplest version would be creature with two hinges.

Don't think of it pushing liquid out of the way!



Approaches to swimming

Several approaches to swimming:

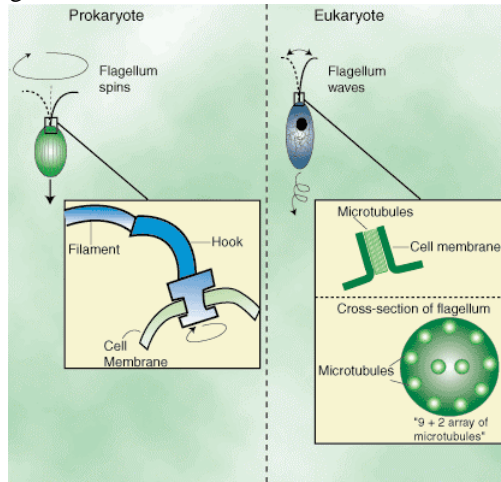
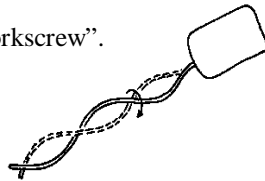
Toroidal motion.



The flexible oar.

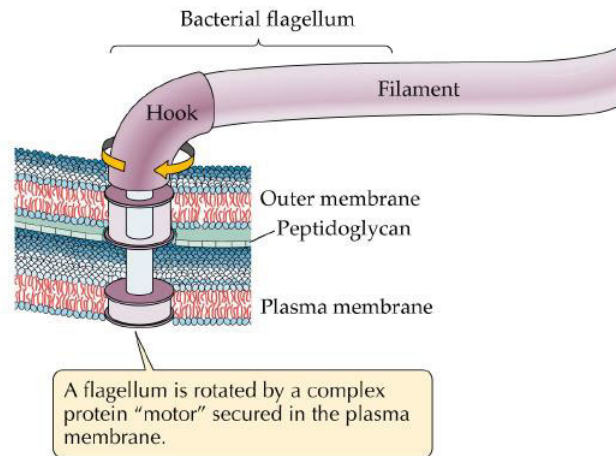


The "corkscrew".



sparksnotes.com

Rotating flagella



Rotating flagella

- Do not think of just a simple corkscrew: that would mean that each rotation of the flagellum would propel the bacterium forward by exactly one "wavelength".
- Real life: the corkscrew is "slipping", so its projection down into the plane does vary each rotational period.
- Typical flagellum is ~ 13 nm in diameter (!), made from protein called flagellin.
- Very clever work done to figure out if *E. Coli* actually rotates its flagellum or not.

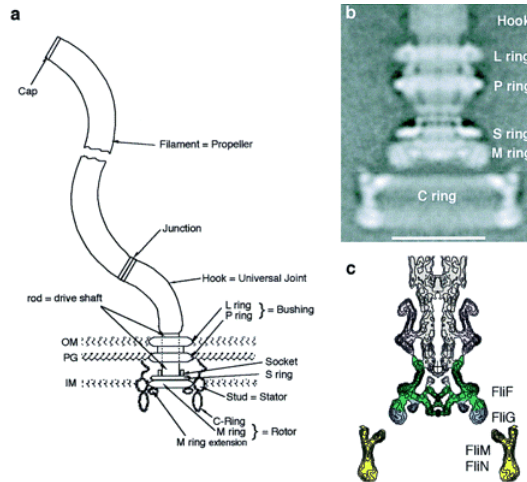
A real biomotor

Derosier, *Cell* **93**, 17 (1998)

Motor is essentially a collection of complicated proteins.

Some of these proteins are “motor proteins”, enzymes that break down ATP into ADP + wastes.

The excess energy liberated is converted into torque (pushing S-ring with respect to the stator).



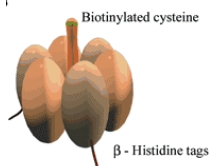
A real biomotor

Even smaller proteins can be rotary motors.

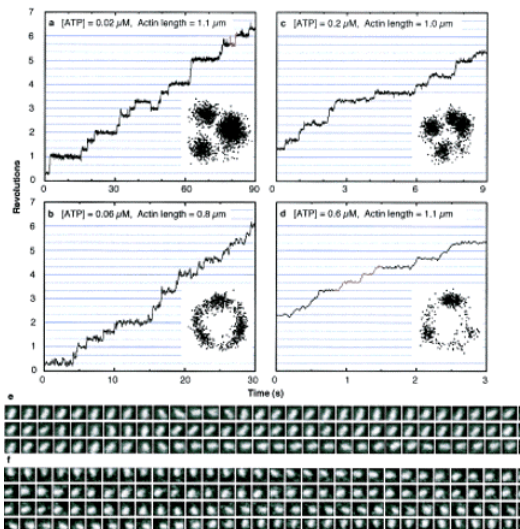
Here is a diagram specifically of F_1 -ATPase, part of ATP-synthase.

The central shaft is torqued during consumption of ATP.

120 degree step per hydrolysis of 1 ATP.



Soong *et al.*, *Science* **290** 1555 (2000)



Yasuda *et al.*, *Cell* **93** 1117 (1998)

How does the flagellum work?

Key: at low Re , everything is *linear*. Can relate torque and force to speed and angular velocity:

$$\begin{aligned} F &= Av + B\Omega \\ N &= Cv + D\Omega \end{aligned} \quad P \equiv \begin{pmatrix} A & B \\ C & D \end{pmatrix}$$

Allowing two screws on the same shaft far from one another, the propulsive matrices should add.

Can prove that the propulsive matrix must be symmetric.

Then consider two identical oppositely pitched corkscrews on the same shaft, falling vertically.

Should be no net torque, but twice the force from just one screw:

P must be diagonal for this case.

Efficiency

Will be proportional to the square of the off-diagonal element of the propulsive matrix P , roughly.

$$\text{Propulsive efficiency} \propto B^2$$

$$B \propto \left(\frac{\text{transverse drag}}{\text{longitudinal drag}} - 1 \right)$$

Can get this by arguing about energy consumption.

Physical origin of that matrix element: related to ratio of transverse drag to longitudinal drag on the flagellum.

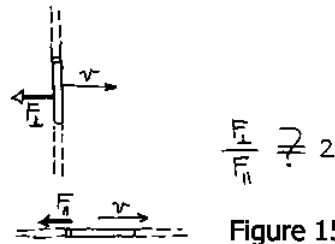


Figure 15

If the drag forces per unit length exactly balanced, there'd be no way of getting net progress forward.

Energy requirements and numbers

Efficiency works out to be around 1% for a round blob and a typical corkscrew flagellum.

Work out the numbers for our 1 micron spherical blob:

Energy intake $\sim 100 \times (F_d \times v)$

$$F_d \sim 6\pi\eta\mu L \sim 5 \times 10^{-13} \text{ N}$$

$$\longrightarrow \text{input power} \sim 1.7 \times 10^{-15} \text{ W}$$

Power density $\sim 0.5 \text{ W / kg}$ (pretty low). 2-3 orders of magnitude lower than power density under load for your laptop battery.

Amount of energy released in hydrolyzing 1 ATP molecule
 $\sim 8 \times 10^{-20} \text{ J}$ ($\sim 80 \text{ pN}\cdot\text{nm}$, or 0.5 eV)

So, would have to be consuming ~ 20000 ATP molecules per second.

Energy requirements and numbers

Is it reasonable to be getting 20000 ATP molecules per second?

Breakdown of a nutrient molecule can produce lots of ATP.

Turns out the food concentration only has to be $\sim 1 \text{ nM}$ for there to be sufficient food available.

Note that the limiting problem here is that food has to *diffuse* to the bacterium!

The immediate environment (as far as continuum fluids is concerned) gets dragged along with the bacterium. New food didn't diffuse in, the bacterium would eat up all the food in its immediate environment and die.

Efficiency of diffusion vs. swimming: "stirring number"

$$S \equiv \frac{l^2 / D}{l/v} = \frac{lv}{D}$$

Does it make sense to seek out food?

Stirring vs. Diffusion


time for transport by stirring: $\frac{l}{v}$

time for transport by diffusion: $\frac{l^2}{D}$

stirring works if $\frac{lv}{D} > 1$

$$S = \frac{lv}{D} \quad \left[R = \frac{lv}{v} \right]$$

$\leftarrow 10^{-5} \text{ cm}^2/\text{sec} \quad \leftarrow 10^2 \text{ cm}^2/\text{sec}$

 $S \approx 10^{-2}$

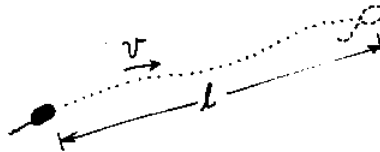
local stirring accomplishes nothing

Local stirring does not, by itself, bring more food to the bacterium.

However, it is possible for the bacterium to swim somewhere where more food is.

Can it swim faster than diffusion?
Yes, for reasonable numbers....

Does it make sense to seek out food?



to out-swim diffusion:

$$l \geq D/v$$

if $D = 10^{-5} \text{ cm}^2/\text{sec}$, $v = .003 \text{ cm}/\text{sec}$

$$l \geq 30 \mu$$

"If you don't swim that far you haven't gone anywhere."

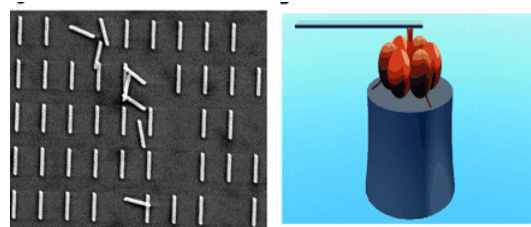
Interfacing biomotors with technology

Hopefully this has been an interesting diversion for you.

Why is it at all relevant?

Recent work on incorporating molecular motors into engineered devices.

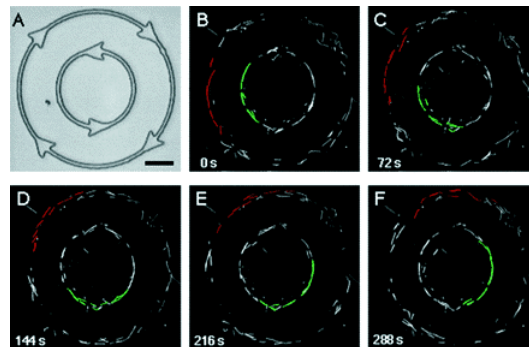
Example: F_1 -ATPase to rotate nanoscale Ni wires:



Soong *et al.*, *Science* **290** 1555 (2000)

Interfacing biomotors with technology

Second example: patterning of surfaces to control movement of actin fibers and microtubules by selective deposition of kinesin.



Hiratsuka *et al.*, *Biophys. J.* **81** 1555 (2001)