Some More on Curve Motion

Returning to our two-dimensional problems of curve motion, we observe that the general equation of motion can be written as

$$\boxed{\mathbf{r}_t = U\hat{\mathbf{n}} + W\hat{\mathbf{t}}}$$

where $U = U(\mathbf{r}, \kappa, \ldots)$ and $W = W(\mathbf{r}, \kappa, \ldots)$ are the normal and tangential velocities. This is an *intrinsic* equation of motion. If we calculate the time derivative of the tangent vector we obtain

$$\frac{\partial \hat{\mathbf{t}}}{\partial t} = \frac{\partial}{\partial t}\frac{1}{\sqrt{g}}\mathbf{r}_\alpha = \frac{\mathbf{r}_{\alpha t}}{\sqrt{g}} - \frac{\mathbf{r}_\alpha}{2g^{3/2}}2\mathbf{r}_\alpha \cdot \mathbf{r}_{\alpha t} = \partial_s \mathbf{r}_t - \hat{\mathbf{t}}\hat{\mathbf{t}} \cdot \partial_s \mathbf{r}_t$$

Now, writing

$$\begin{aligned}\hat{\mathbf{t}} &= \cos\theta\hat{\mathbf{e}}_x + \sin\theta\hat{\mathbf{e}}_y \\ \hat{\mathbf{n}} &= \sin\theta\hat{\mathbf{e}}_x - \cos\theta\hat{\mathbf{e}}_y\end{aligned}$$

we see that $\partial\hat{\mathbf{t}}/\partial t = -\theta_t\hat{\mathbf{n}}$, so

$$\boxed{\theta_t = -U_s + \kappa W}$$

Curve Motion - continued

Previously, we saw that if a curve moves according to the intrinsic equation of motion

$$\boxed{\mathbf{r}_t = U\hat{\mathbf{n}} + W\hat{\mathbf{t}}}$$

then the tangent angle evolves as

$$\boxed{\theta_t = -U_s + \kappa W \ .}$$

With a bit more work it is straightforward to show that the curvature itself obeys the PDE

$$\boxed{\kappa_t = -\left(\partial_{ss} + \kappa^2\right) U + \kappa_s W \ .}$$

These two results indicate that there are intrinsic *geometrical nonlinearities* due to the fact that the vector $\mathbf{r}$ and the arclength s are not independent. Note also that in many ways the tangential velocity is something we can choose (like a gauge), as it corresponds to a particular time-dependent parameterization.

Consider *motion by mean curvature* in the simplest case of 2-D motion,

$$\boxed{U = -\gamma\kappa \quad \text{and} \quad W = 0 \ .}$$

Curve Motion - continued

This corresponds to an energy functional $\mathcal{E} = \gamma L$, for which the tangent angle and curvature evolve as

$$\boxed{\theta_t = -U_s + \kappa W = \gamma \theta_{ss} \;, \qquad \kappa_t = \gamma \left(\kappa_{ss} + \kappa^3 \right) \;.}$$

Since we derived this by a variational principle from the energy functional $\mathcal{E}$, it stands to reason that $\mathcal{E}$ is driven downhill. To check this we compute

$$\frac{\partial \mathcal{E}}{\partial t} = \gamma \int d\alpha \frac{1}{2} \frac{1}{\sqrt{g}} 2\mathbf{r}_\alpha \cdot \mathbf{r}_{\alpha t} = \gamma \int ds \hat{\mathbf{t}} \cdot \partial_s \mathbf{r}_t$$

Since $\mathbf{r}_t = -\gamma \kappa \hat{\mathbf{n}}$, $\partial_s \mathbf{r}_t = -\gamma \kappa_s \hat{\mathbf{n}} - \gamma \kappa^2 \hat{\mathbf{t}}$, so

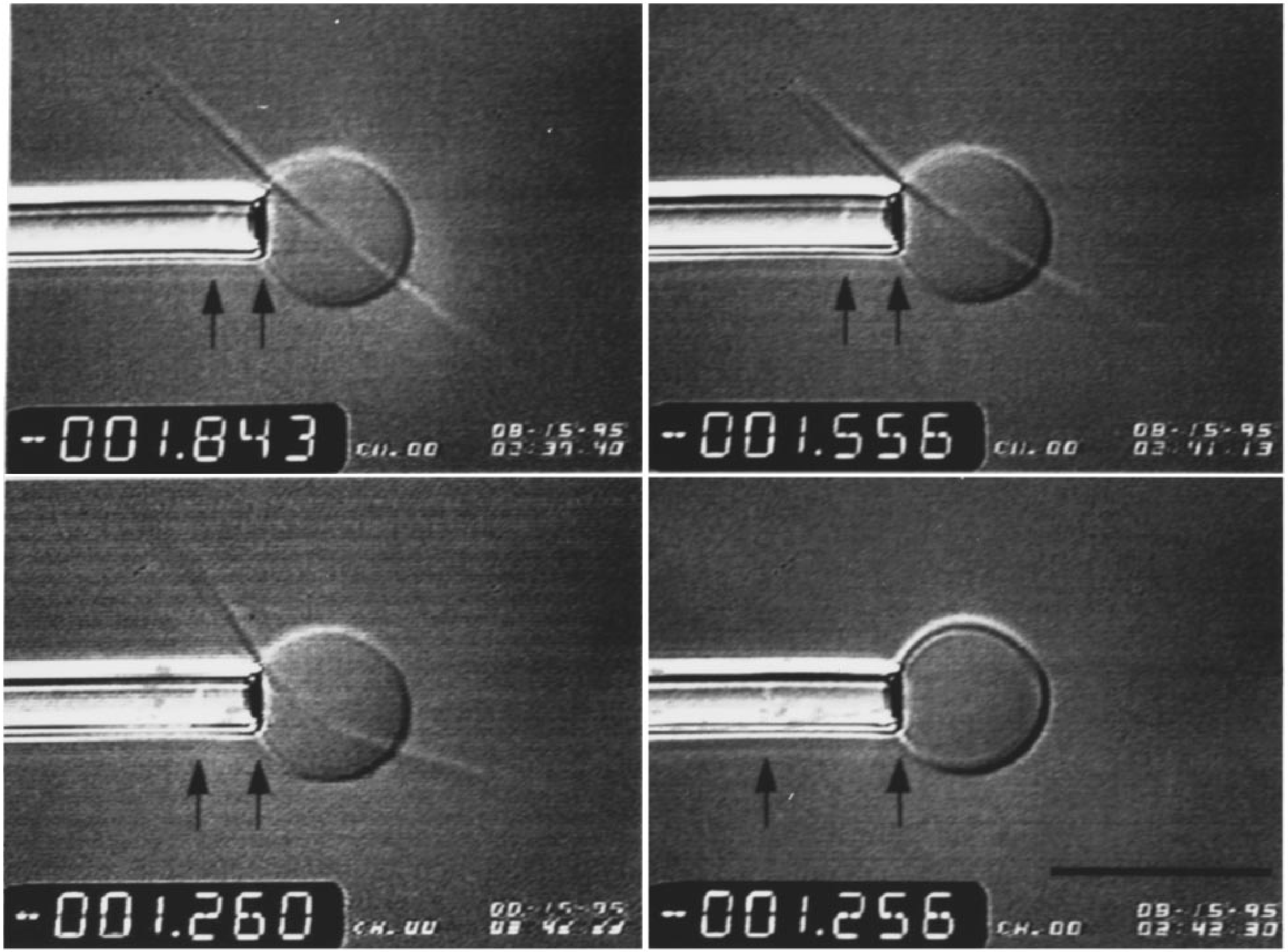
$$\boxed{\frac{\partial \mathcal{E}}{\partial t} = -\gamma^2 \int ds \kappa^2 \leq 0}$$

Thus, the length is driven downhill (the "curve-shortening equation"). It is easy to show that the area A enclosed by a curve evolves as

$$A_t = \int ds U \qquad \text{so, here} \quad \boxed{A_t = -\gamma \int ds \kappa = -2\pi\gamma \;.}$$

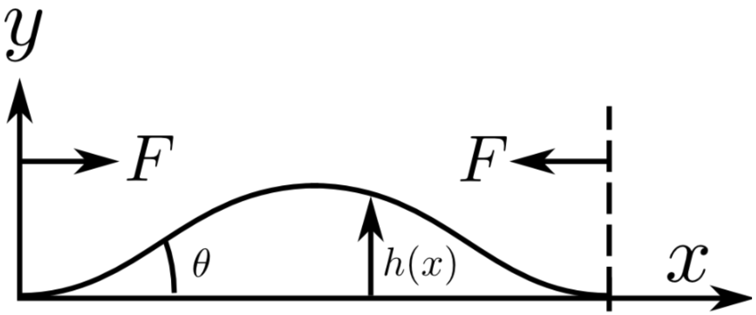
So the area vanishes in a finite time!

Buckling Microtubules in Vesicles



Fygenson, et al, *PRE* **55**, 850 (1997)

Euler Buckling



Here we consider the classic problem of *Euler buckling*, in which an elastic filament subject to thrusting forces at its ends deforms at a critical force.

The energy functional associated with this configuration is just

$$\boxed{\mathcal{E}[\theta] = \int_0^L ds \left[\frac{A}{2}\theta_s^2 + F\cos\theta \right]}$$

where the second term represents the work done by the force in moving the end,

$$X(L) - X(0) = \int_0^L \frac{dx}{ds} ds = \int_0^L \cos\theta(s)$$

where the components of the curve in the x, y directions are just

$$\begin{pmatrix} dx/ds \\ dy/ds \end{pmatrix} = \begin{pmatrix} \cos\theta(s) \\ \sin\theta(s) \end{pmatrix}$$

Euler Buckling - continued

The equilibrium condition is

$$\frac{\delta \mathcal{E}}{\delta \theta} = 0 = -\frac{d}{ds}\frac{\partial \cdots}{\partial \theta_s} + \frac{\partial \cdots}{\partial \theta} \quad \rightarrow \boxed{A\theta_{ss} + F \sin\theta = 0 \ ,}$$

otherwise known as the pendulum equation. [Think of $\mathcal{L} = \mathcal{T} - \mathcal{V}$, with $\mathcal{T} = (1/2)m\dot{q}^2$ and $\mathcal{V} = mg(1 - \cos q)$.] Let us consider *clamped* boundary conditions, $\theta(0) = \theta(L) = 0$. We expect a shape with a single bump in the middle, which is a sin function for θ,

$$\boxed{\theta(s) \simeq a \sin\left(\frac{2\pi s}{L}\right) \ .}$$

This will only solve the linearized Euler-Lagrange equation $\theta_{ss} \simeq -(F/A)\theta$ provided

$$\frac{F}{A} = \frac{4\pi^2}{L^2} \quad \text{or} \quad F = F_c = \frac{4\pi^2 A}{L^2} = \boxed{4\pi^2 \left(\frac{k_B T}{L_p}\right)\left(\frac{L_p}{L}\right)^2}$$

Euler Buckling - continued

Consider microtubules. $L_p \sim 0.1$ cm, and take $L \sim 20\ \mu\text{m} = 2 \times 10^{-3}$ cm (as in expt). Then $L_p/L \sim 50$ and

$$F_c \sim 40 \cdot \left(\frac{4 \times 10^{-14}}{0.1}\right) \cdot (50)^2 \simeq 0.5 \text{ pN}$$

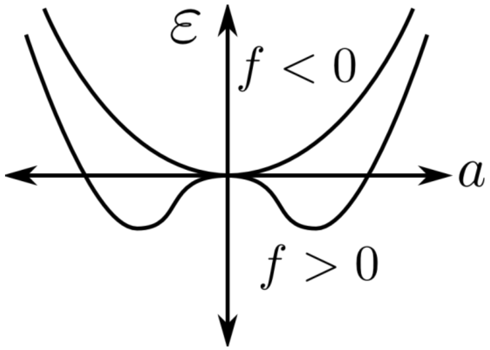
Near the bifurcation, we expect that nonlinearities will stabilize the buckled shape at some finite amplitude. If we continue with the single-mode approximation and variational approach we seek an energy functional of higher-than-quadratic order to achieve this. Expand the force near F_c and the geometric term in the energy,

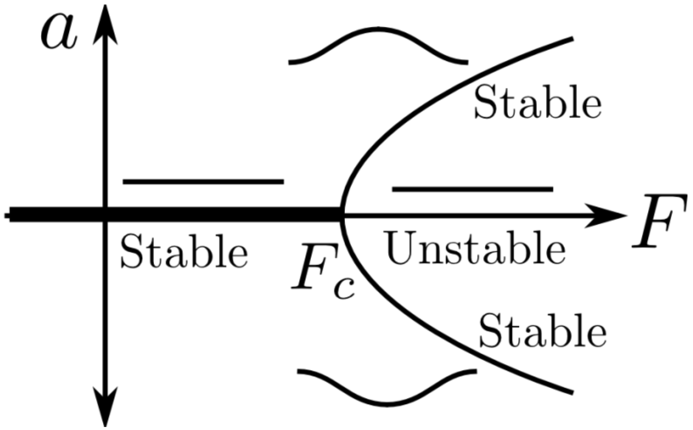
$$F = F_c(1+f) \qquad \cos\theta = 1 - \frac{1}{2}\theta^2 + \frac{\theta^4}{24} + \dots$$

The energy functional is then

$$\begin{aligned}\mathcal{E}[\theta] &\simeq \int_0^L \left[\frac{A}{2}\theta_s^2 + F_c(1+f)\left(1 - \frac{1}{2}\theta + \frac{\theta^4}{24} + \dots\right)\right] \\ &\simeq \mathcal{E}_c + F_c(1+f)L + \frac{F_c L}{2}\left[\frac{-fa^2}{2} + \frac{a^4}{32} + \dots\right]\end{aligned}$$

Post-Buckling Behaviour





Thus, we have a *Landau theory* for the bifurcation, in which the relevant part of the energy functional has the form

$$\boxed{\mathcal{E}[\theta] \simeq \frac{F_c L}{2}\left[\frac{-f a^2}{2} + \frac{a^4}{32} + \dots\right]}$$

When $f < 0$ (below the bifurcation), there is a single minimum at $a = 0$, while above ($f > 0$) there are two minimum at

$$\boxed{a = \pm\sqrt{8f}}$$

the characteristic of a *pitchfork bifurcation.*

Post-Buckling Behaviour - continued

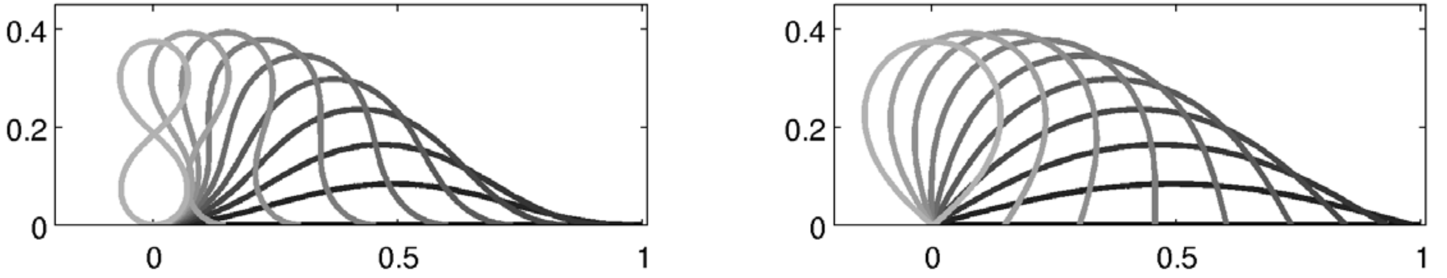
After buckling, the deformed rod behaves like a Hookean spring, whose properties we can find by comparing the compression length to the applied force. The difference in length (from before) is just

$$X(L) - X(0) = \int_0^L ds \cos\theta \simeq \int_0^L ds \left(1 - \frac{1}{2}\theta^2 + \ldots\right) \simeq L - \frac{La^2}{4} + \ldots$$

So, the displacement due to a force beyond F_c is $La^2/4$. With the knowledge that $a = \sqrt{8f}$,

$$\Delta x \simeq \frac{L}{4} 8f = 2L\left(\frac{F - F_c}{F_c}\right) \qquad \Longrightarrow \qquad \boxed{F - F_c = \frac{F_c}{2L}\Delta x}$$

Thus, beyond the critical force the rod behaves as a spring with effective spring constant $F_c/2L$. Solutions farther from the bifurcation are possible through a numerical approach. For clamped ends (left) and hinged ends (right) we obtain



Chemical Kinetics and Pattern Formation

The key article on pattern formation that started the field was by Alan Turing. He showed that the combination of nonlinear chemical kinetics and diffusion can produce patterns, e.g. stationary patterns in time. These were finally observed experimentally decades after the prediction. We need first to understand the basic laws of mass action for chemical reactions.

Michaelis-Menten kinetics. The essential idea behind this simple model of enzyme-substrate dynamics is the reaction scheme

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

where E is the enzyme, S is the substrate, P is the product, and ES is the enzyme-substrate complex. k_1, k_{-1}, k_2 are the rate constants (empirically measured quantities). For notation, let $s = [S], e = [E], c = [ES], p = [P]$. The concentration is defined as the average concentration (for a CSTR). The law of mass action is then that the reaction rate is proportional to the concentration or products of concentrations for bilinear reactions.

Michaelis-Menten Kinetics - continued

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES \xrightarrow{k_2} E + P$$

The chemical rate equations are

$$\begin{aligned}
\frac{de}{dt} &= -k_1 es + k_{-1} c + k_2 c \\
\frac{ds}{dt} &= -k_1 es + k_{-1} c \\
\frac{dc}{dt} &= k_1 es - k_2 c - k_{-1} c \\
\frac{dp}{dt} &= k_2 c
\end{aligned}$$

The initial conditions are

$$s(0) = s_0 \qquad c(0) = 0 \qquad e(0) = e_0 \qquad p(0) = 0$$

Note that p is completely decoupled from the other reactions, so that

$$p(t) = k_2 \int_0^t c(t')dt'$$

Michaelis-Menten Kinetics - continued

It also follows that the quantity $e + c$ must also be conserved (conservation of the enzyme/catalyst), so that

$$\frac{de}{dt} + \frac{dc}{dt} = 0$$

which is indeed satisfied. Thus, $e + c = e_0$ at all times. The system thus reduces from four coupled differential equations to just two

$$\begin{aligned} \frac{ds}{dt} &= -k_1 e_0 s + (k_1 s + k_{-1})c & \qquad s(0) &= s_0 \\ \frac{dc}{dt} &= k_1 e_0 s - (k_1 s + k_{-1} + k_2)c & \qquad c(0) &= 0 \end{aligned}$$

It is useful to identify appropriate scalings. The concentration of the enzyme/catalyst is generally much smaller concentration of the substrate, so that a small parameter is $\epsilon = e_0/s_0$. Let the rescaled time be $\tau = k_1 e_0 t$, and

$$\begin{aligned} u(\tau) &= s(t)/s_0 & \qquad \lambda &= \frac{k_2}{k_1 s_0} \\ v(\tau) &= c(t)/e_0 & \qquad k &= \frac{k_{-1} + k_2}{k_1 s_0} \end{aligned}$$

Michaelis-Menten Kinetics - continued

The equation system thus reduces further to an equation for the substrate and the complex:

$$\begin{aligned} \frac{du}{d\tau} &= -u + (u + k - \lambda)v & \qquad u(0) &= 1 \\ \epsilon \frac{dv}{d\tau} &= u - (u + k)v & \qquad v(0) &= 0 \end{aligned}$$

Although ϵ is small, neglecting it would remove the highest time derivative in one equation, and is thus a singular perturbation.

See Matlab program Michaelis_Menten.m

Michaelis-Menten Kinetics - continued

Naive method of solution Suppose that $\epsilon \ll 1$. Then we can assume the second equation (for the complex) will rapidly reach a quasi-equilibrium in which $dv/d\tau \sim 0$, and so

$$0 = u - (u + k)v \quad \text{or} \quad v = \frac{u}{u + k} \ .$$

In unscaled units this is

$$k_1 es \sim (k_{-1} + k_2)c \qquad e = e_0 - c \qquad c = e_0 \frac{s}{s + K_m}$$

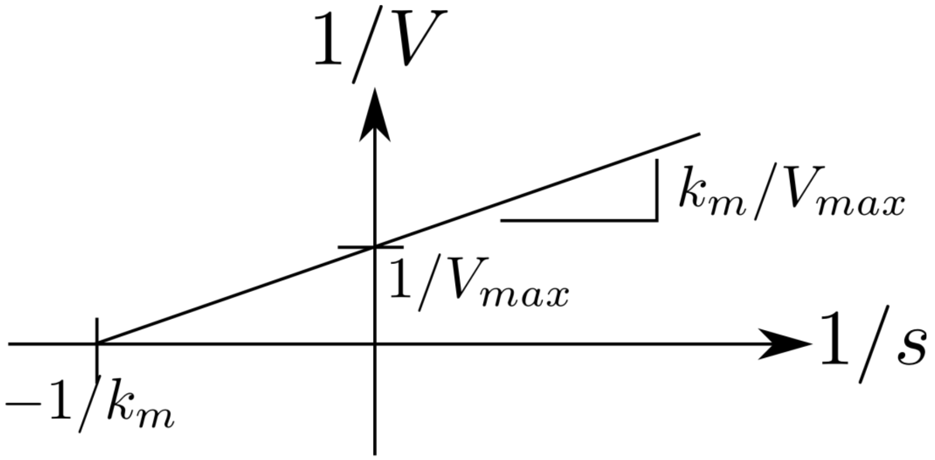
where $K_m = (k_2 + k_{-1})/k_1$. However, this only works if there is a large separation in time scales between the two reactions. The "fast" variable is then coupled to the slow one, which obeys a nonlinear relation. The rate of reaction would then be

$$\frac{dp}{dt} \equiv V = k_2 c = k_2 e_0 \frac{s}{s + K_m} = V_{\max} \frac{s}{s + K_m} \ .$$

The unknown constants K_m and $V_{\max}$ are determined from a plot of $1/V = (1 + K_m/s)/V_{max}$ vs $1/s$

Michaelis-Menten Kinetics - continued

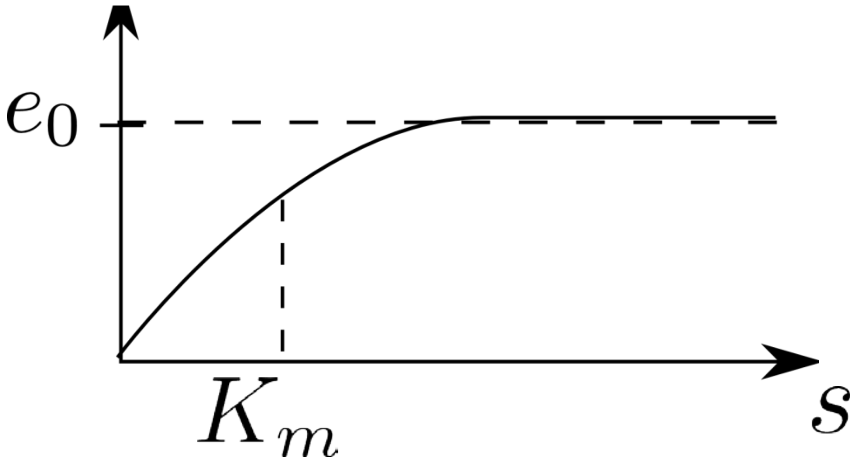
This is the so-called *Lineweaver-Burk plot*.



The fundamental result of slaving the fast variable to the slow one is to create this very nonlinear dependence of the reaction rate on the substrate concentration:

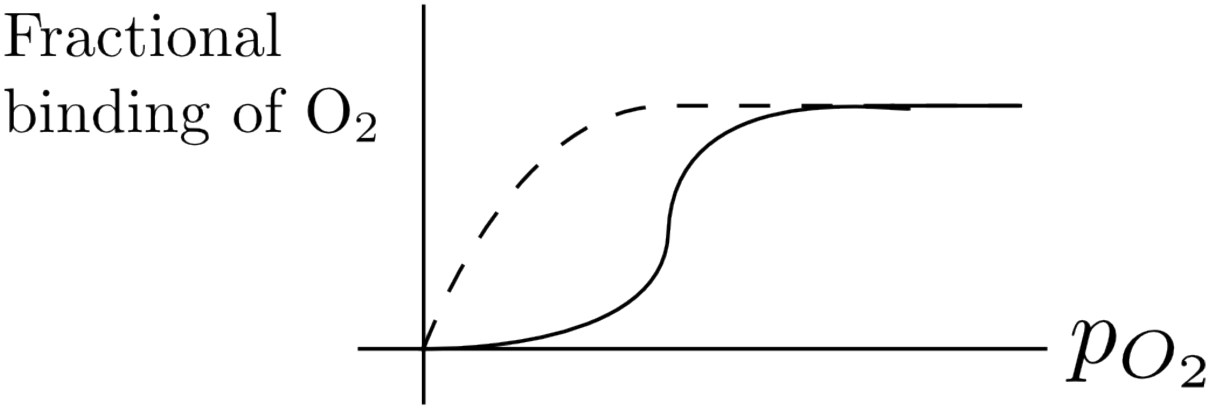
$$\frac{dp}{dt} = k_2 c$$

$$c = e_0 \frac{s}{s + K_m}$$



Cooperativity in Reaction Rates

This is an example of a "non-cooperative" reaction. Cooperativity arises from e.g. initial binding effects altering the probability/kinetics of subsequent binding, as with oxygen and hemoglobin. The binding of oxygen to hemoglobin involves a tetramer of four proteins that each bind oxygen. The binding of each site is linked to the number of bound oxygens, so that the second oxygen is easier to bind than the first, and so on. This allows for cooperativity and very large change in absorbed oxygen over a relatively small shift in oxygen concentration (perfectly tuned for lungs).



This is essentially a *switch*.