### Fast/slow dynamical systems and chemical reaction kinetics

0. **Reading from Logan**: Sections 2.5.1-2 and 3.4.1-2
   (and 1.3.2, 2.1-2.3 if needed for further background on phase planes).
   For further background on chemical reaction kinetics, see Chapter 3 of Mark H Holmes' *Introduction to the Foundations of Applied Mathematics* (Duke Library e-Book), or Chapter 1 of J. Keener and J. Sneyd's *Mathematical Physiology, Vol I* (e-Book).

1. Problem 3 from Logan Exercises for Section 3.4.2, page 200. ("Find a uniformly valid approximation to the problem...$\epsilon y'' + \cdots$") (or see page 134, problem 3 if you have Logan's 3rd Edition).

2. See the plot of the numerically computed limit cycle solution $x(t)$ of the ODE:

$$\frac{1}{2}\frac{d^2x}{dt^2} + (3x^2 - 6x - 9)\frac{dx}{dt} + 4x = 0.$$
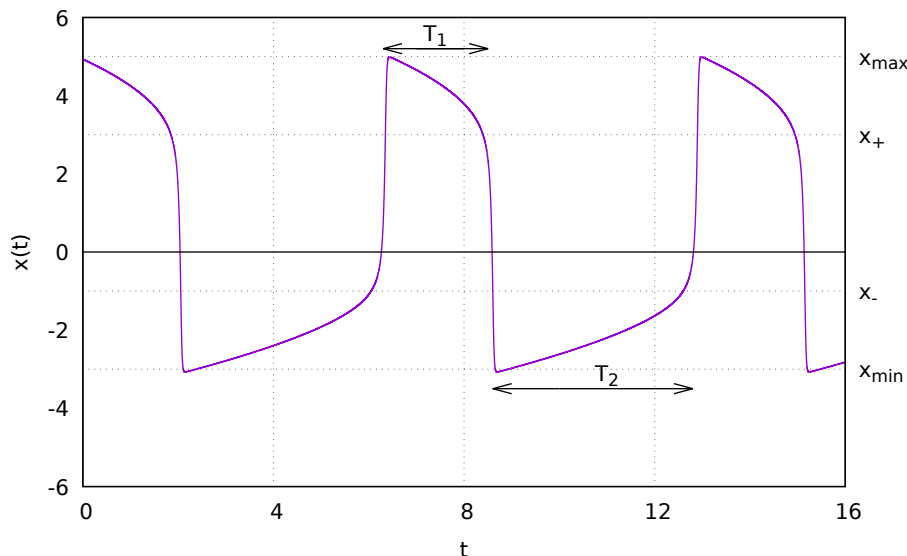
(a) Explain how this ODE can be written as a Liénard phase plane system in the form

$$\epsilon\frac{dx}{dt} = f(x) + 4y, \qquad \frac{dy}{dt} = -x. \qquad\qquad \text{(What are} \epsilon, f(x), y)?$$

(b) For $\epsilon \to 0$ determine the leading order estimates for the key values: $x_{\min}, x_-, x_+, x_{\max}$.

(c) Determine the leading order estimate for the period of oscillation of the limit cycle, $P \sim T_1 + T_2$.
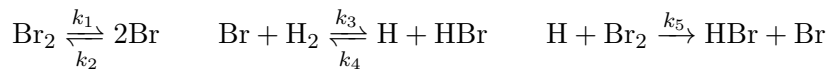   Hint: Obtain the time spent moving along segments as

$$T = \int_{t_{\text{start}}}^{t_{\text{end}}} dt = \int_{x_{\text{start}}}^{x_{\text{end}}} \frac{dx}{g(x)} \qquad\qquad \text{where} \quad \frac{dx}{dt} = g(x)$$

and recall HW2Q6 part c.

(continued)

3. <u>The Quasi-Steady-State Assumption</u> (QSSA) In chemistry, a short-cut to doing scaling and slow/fast perturbation analysis is to jump ahead to the leading order slow equations using the assumption that the rate of production of all intermediate compounds equilibrates instantaneously (i.e. those rate equations reduce to steady algebraic relations, like $\epsilon \frac{dc}{dt} = 0$).

Use the QSSA approach to consider the overall reaction for the formation of hydrogen-bromide: $H_2 + Br_2 \rightarrow 2HBr$. This reaction takes place through several steps:

$$Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2Br \qquad Br + H_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} H + HBr \qquad H + Br_2 \overset{k_5}{\longrightarrow} HBr + Br$$

Consider the atomic forms H and Br to be unstable intermediates (similar to complexes being unstable intermediates). Apply the QSSA to obtain the <u>dimensional</u> rate law for the production of HBr

$$\frac{d[HBr]}{dT} = \frac{\alpha[H_2][Br_2]^{3/2}}{[Br_2] + \beta[HBr]}.$$

(a) Write the system of rate equation for the evolution of each chemical.

(b) Find α, β.

For writing your equations, call the variables for the concentrations of the different chemical species: $A = [H_2], B = [Br_2], C = [Br], D = [H], P = [HBr]$ (P for product).[1]

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[1] "[X]" is the usual chemistry textbook notation for "concentration of chemical X".