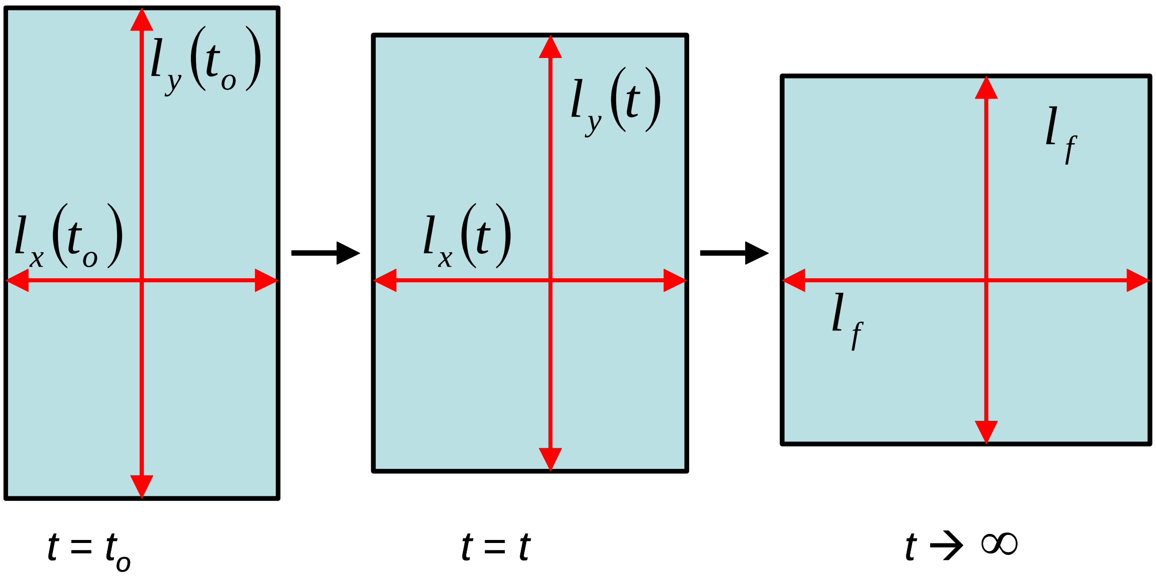
ChE/MSE 505: Final Examination
Administered: Friday, December 7, 2007

Problem (1)

Consider a crystalline material of density, ρ, that has initial dimensions $l_x(t_o)$ and $l_y(t_o)$. This material has a high (unfavorable) surface energy and therefore would like to change its shape (through diffusion or convection, the actual physical mechanism doesn't matter for this problem) to a shape that has the minimum perimeter, namely $l_x(t \to \infty) = l_y(t \to \infty) = l_f$. This process is illustrated in the figure below.



The rate of change of the perimeter, $P(t) = 2l_x(t) + 2l_y(t)$, can be assumed to follow a first order rate law.

$$\frac{dP}{dt} = -\frac{1}{\tau}\left[P(t) - P_f\right]$$

where τ is the characteristic relaxation time associated with the process (assume τ is constant) and P_f is the perimeter at infinite time, $P_f = 4l_f$. This relaxation process occurs under the constraint of conservation of mass. The mass of the system at any time is given by

$$M = \rho A(t) = \rho\left[l_x(t) l_y(t)\right]$$

where $A(t)$ is the area of the material, $A(t) = l_x(t) l_y(t)$. From the conservation of mass, we know that the mass at the initial time and at infinite time are the same

$$M(t_o) = \rho\left[l_x(t_o) l_y(t_o)\right] = M(t \to \infty) = \rho\left[l_f^2\right]$$

Equating these, we can solve for l_f which is a parameter in the rate law.

$$l_f = \sqrt{l_x(t_o) l_y(t_o)}$$

This is the complete information required to describe the evolution of the material shape in time. Based on this information, answer the following questions.

Solution Approach Number 1.

(a) What kind of equations (AE, ODE, PDE or IE) do you have in this system?

We have one ordinary differential equation and one algebraic equation.

(b) What is the independent variable in this system?

The independent variable is time, *t*.

(c) What are the dependent variables that must be solved for in this system?

Since we have two equations, we can only have two dependent variables. In the equations above we see four variables that are functions of time, $A(t)$, $P(t)$, $l_x(t)$, and $l_y(t)$. But the area and the perimeter are simply functions of $l_x(t)$ and $l_y(t)$:

$$P(t) = 2l_x(t) + 2l_y(t)$$

and

$$A(t) = l_x(t) l_y(t)$$

$A(t)$ and $P(t)$ can be eliminated via simple substitution. Therefore, the two dependent variables that we should solve for are $l_x(t)$ and $l_y(t)$.

(d) Are the equations linear or nonlinear in the unknowns?

The ODE is linear and the AE is nonlinear.

(e) What are the equations in terms of the dependent variables that must be solved for in this system?

If we substitute into the equations, we obtain

$$2\frac{dl_x(t)}{dt}+2\frac{dl_y(t)}{dt}=-\frac{1}{\tau}\left[2l_x(t)+2l_y(t)-4l_f\right]$$

$$M=\rho\left[l_x(t)l_y(t)\right]$$

(f) Convert the system of equations into a form that you know how to numerically solve.

When faced with a combined set of ODEs and AEs, one simple trick is to differentiate the AEs and convert it to an ODE. In this case, since the mass, M, is constant, this leads to

$$0=l_x(t)\frac{dl_y(t)}{dt}+l_y(t)\frac{dl_x(t)}{dt}$$

So now we have a system of two ODEs. We know how to solve this numerically if we can isolate the derivatives on the LHS. This can be done through substitution. We rearrange the mass balance to yield

$$\frac{dl_y(t)}{dt}=-\frac{l_y(t)}{l_x(t)}\frac{dl_x(t)}{dt}$$

We substitute this into the rate expression and simplify:

$$2\frac{dl_x(t)}{dt}-2\frac{l_y(t)}{l_x(t)}\frac{dl_x(t)}{dt}=-\frac{1}{\tau}\left[2l_x(t)+2l_y(t)-4l_f\right]$$

$$\frac{dl_x(t)}{dt}=\frac{-\frac{1}{\tau}\left[l_x(t)+l_y(t)-2l_f\right]}{1-\frac{l_y(t)}{l_x(t)}}$$

If we substitute this expression back into the equation for $\frac{dl_y(t)}{dt}$ we find,

$$\frac{dl_y(t)}{dt}=\frac{\frac{1}{\tau}\left[l_x(t)+l_y(t)-2l_f\right]}{\frac{l_x(t)}{l_y(t)}-1}$$

Therefore, we have a set of two coupled, nonlinear ODEs of the form:

$$\frac{dl_x(t)}{dt}=\frac{-\frac{1}{\tau}l_x(t)\left[l_x(t)+l_y(t)-2l_f\right]}{l_x(t)-l_y(t)}$$

$$\frac{dl_y(t)}{dt}=\frac{\frac{1}{\tau}l_y(t)\left[l_x(t)+l_y(t)-2l_f\right]}{l_x(t)-l_y(t)}$$

which is of the form

$$\frac{d\underline{y}}{dt}=\underline{f}(\underline{y})$$

which we certainly know how to solve.

(g) What conditions (initial conditions or boundary conditions) are required to solve this problem? What are they?

We require two initial conditions. They are $l_x(t_o)$ and $l_y(t_o)$.

(h) What numerical technique would use you to solve this problem?

I would use the fourth-order Runge-Kutta method.

(i) Show that $l_x(t\to\infty)=l_y(t\to\infty)=l_f$ is indeed a critical point of the system.

To find a critical point, we must solve

$$\frac{d\underline{y}}{dt}=\underline{f}(\underline{y})=\underline{0}$$

which in our case is explicitly,

$$\frac{-\frac{1}{\tau}l_x(t)\left[l_x(t)+l_y(t)-2l_f\right]}{l_x(t)-l_y(t)}=0$$

$$\frac{\frac{1}{\tau}l_y(t)\left[l_x(t)+l_y(t)-2l_f\right]}{l_x(t)-l_y(t)}=0$$

Interestingly, we see that both of these equations are undetermined (0/0) at the root. This is problematic. We need to find a form of the equations where the equations are not undetermined at the critical point.

We know that the equations are consistent with the original two equations, the rate law and the conservation of mass constraint.

$$2\frac{dl_x(t)}{dt} + 2\frac{dl_y(t)}{dt} = -\frac{1}{\tau}\left[2l_x(t) + 2l_y(t) - 4l_f\right]$$

$$M = \rho\left[l_x(t)l_y(t)\right]$$

This form looks more amenable. We set the derivatives to zero and obtain two algebraic equations.

$$0 = -\frac{1}{\tau}\left[2l_x(t_{ss}) + 2l_y(t_{ss}) - 4l_f\right]$$

$$M = M(t_o) = \rho\left[l_x(t_{ss})l_y(t_{ss})\right]$$

Solving the first equation analytically, we have

$$l_y(t_{ss}) = 2l_f - l_x(t_{ss}) = 2\sqrt{l_x(t_o)l_y(t_o)} - l_x(t_{ss})$$

Substituting into the second equation yields

$$\rho\left[l_x(t_o)l_y(t_o)\right] = \rho\left[l_x(t_{ss})\left[2\sqrt{l_x(t_o)l_y(t_o)} - l_x(t_{ss})\right]\right]$$

Solving for $l_x(t_{ss})$ yields a quadratic polynomial

$$l_x(t_{ss})^2 - 2\sqrt{l_x(t_o)l_y(t_o)}\,l_x(t_{ss}) + l_x(t_o)l_y(t_o) = 0$$

Using the quadratic equation we find

$$l_x(t_{ss}) = \frac{2\sqrt{l_x(t_o)l_y(t_o)} \pm \sqrt{4l_x(t_o)l_y(t_o) - 4l_x(t_o)l_y(t_o)}}{2} = \sqrt{l_x(t_o)l_y(t_o)}$$

Consequently,

$$l_y(t_{ss}) = 2\sqrt{l_x(t_o)l_y(t_o)} - l_x(t_{ss}) = 2\sqrt{l_x(t_o)l_y(t_o)} - \sqrt{l_x(t_o)l_y(t_o)} = \sqrt{l_x(t_o)l_y(t_o)}$$

(j) Determine the stability of the critical point and the type of critical point.

Not done for solution approach number one.

Solution Approach Number 2.

(a) What kind of equations (AE, ODE, PDE or IE) do you have in this system?

We have one ordinary differential equation and one algebraic equation.

(b) What is the independent variable in this system?

The independent variable is time, *t*.

(c) What are the dependent variables that must be solved for in this system?

In the equations above we see four variables that are functions of time, $A(t)$, $P(t)$, $l_x(t)$, and $l_y(t)$. From one point of view, only one of these variables is independent, because we have three algebraic constraints

$$P(t) = 2l_x(t) + 2l_y(t)$$

and

$$A(t) = l_x(t)l_y(t)$$

and

$$M(t_o) = \rho\left[l_x(t_o)l_y(t_o)\right] = M(t) = \rho\left[l_x(t)l_y(t)\right]$$

We can express $A(t)$, $P(t)$ and $l_y(t)$ in terms of $l_x(t)$.

$$l_y(t) = \frac{l_x(t_o)l_y(t_o)}{l_x(t)}$$

$$A(t) = l_x(t_o)l_y(t_o)$$

$$P(t) = 2l_x(t) + 2\frac{l_x(t_o)l_y(t_o)}{l_x(t)}$$

Therefore, there is only one dependent variables that we should solve for, and it is $l_x(t)$.

(d) Are the equations linear or nonlinear in the unknowns?

If we express the ODE in terms of a single dependent variable, we have

$$\frac{dP}{dt} = -\frac{1}{\tau}\left[P(t) - P_f\right]$$

$$\left[2 - 2\frac{l_x(t_o)l_y(t_o)}{l_x^2(t)}\right]\frac{dl_x(t)}{dt} = \frac{-\frac{1}{\tau}\left[2l_x(t) + 2\frac{l_x(t_o)l_y(t_o)}{l_x(t)} - 4\sqrt{l_x(t_o)l_y(t_o)}\right]}{}$$

Simplifying we have

$$\frac{dl_x(t)}{dt} = \frac{-\frac{1}{\tau}l_x^2(t)\left[l_x(t) + \frac{l_x(t_o)l_y(t_o)}{l_x(t)} - 2\sqrt{l_x(t_o)l_y(t_o)}\right]}{l_x^2(t) - l_x(t_o)l_y(t_o)}$$

The ODE is nonlinear.

(e) What are the equations in terms of the dependent variables that must be solved for in this system?

We just have one equation.

$$\frac{dl_x(t)}{dt} = \frac{-\frac{1}{\tau}l_x^2(t)\left[l_x(t) + \frac{l_x(t_o)l_y(t_o)}{l_x(t)} - 2\sqrt{l_x(t_o)l_y(t_o)}\right]}{l_x^2(t) - l_x(t_o)l_y(t_o)}$$

(f) Convert the system of equations into a form that you know how to numerically solve.

The equation is already in a form that we know how to solve. A first order, nonlinear ODE with the differential isolated on the left hand side.

$$\frac{dl_x(t)}{dt} = \frac{-\frac{1}{\tau}l_x^2(t)\left[l_x(t) + \frac{l_x(t_o)l_y(t_o)}{l_x(t)} - 2\sqrt{l_x(t_o)l_y(t_o)}\right]}{l_x^2(t) - l_x(t_o)l_y(t_o)}$$

(g) What conditions (initial conditions or boundary conditions) are required to solve this problem? What are they?

We require two initial conditions. They are $l_x(t_o)$ and $l_y(t_o)$.

(h) What numerical technique would use you to solve this problem?

I would use the fourth-order Runge-Kutta method.

(i) Show that $l_x(t \to \infty) = l_y(t \to \infty) = l_f$ is indeed a critical point of the system.

To find a critical point, we must solve

$$\frac{d\underline{y}}{dt} = \underline{f}(\underline{y}) = \underline{0}$$

which in our case is explicitly,

$$0 = \frac{-\frac{1}{\tau} l_x^2(t)\left[l_x(t) + \frac{l_x(t_o) l_y(t_o)}{l_x(t)} - 2\sqrt{l_x(t_o) l_y(t_o)} \right]}{l_x^2(t) - l_x(t_o) l_y(t_o)}$$

In order for this equation to be zero, the nontrivial solution occurs when the term in the square brackets is zero.

$$0 = l_x(t) + \frac{l_x(t_o) l_y(t_o)}{l_x(t)} - 2\sqrt{l_x(t_o) l_y(t_o)}$$

This can also be rewritten as

$$0 = l_x^2(t) - 2\sqrt{l_x(t_o) l_y(t_o)}\, l_x(t) + l_x(t_o) l_y(t_o)$$

Using the quadratic equation we find

$$l_x(t_{ss}) = \frac{2\sqrt{l_x(t_o) l_y(t_o)} \pm \sqrt{4 l_x(t_o) l_y(t_o) - 4 l_x(t_o) l_y(t_o)}}{2} = \sqrt{l_x(t_o) l_y(t_o)}$$

Consequently,

$$l_y(t_{ss}) = 2\sqrt{l_x(t_o) l_y(t_o)} - l_x(t_{ss}) = 2\sqrt{l_x(t_o) l_y(t_o)} - \sqrt{l_x(t_o) l_y(t_o)} = \sqrt{l_x(t_o) l_y(t_o)}$$

(j) Determine the stability of the critical point and the type of critical point.

When you have only one ODE, the stability of the critical point is determined by the sign of the coefficient.

Our ODE is given by:

$$\frac{dl_x(t)}{dt} = f(l_x(t))$$

where $f(l_x(t)) = \dfrac{-\frac{1}{\tau}\left[l_x^3(t) - 2l_x^2(t)\sqrt{l_x(t_o)l_y(t_o)} + l_x(t_o)l_y(t_o)l_x(t)\right]}{l_x^2(t) - l_x(t_o)l_y(t_o)}$

If we linearize this expression, we have

$$\frac{dl_x(t)}{dt} = \left.\frac{df}{dl_x(t)}\right|_t l_x(t)$$

$$\frac{df}{dl_x(t)} = \frac{-\frac{1}{\tau}\left[3l_x^2(t) - 4l_x(t)\sqrt{l_x(t_o)l_y(t_o)} + l_x(t_o)l_y(t_o)\right]}{l_x^2(t) - l_x(t_o)l_y(t_o)} - \frac{-\frac{1}{\tau}\left[l_x^3(t) - 2l_x^2(t)\sqrt{l_x(t_o)l_y(t_o)} + l_x(t_o)l_y(t_o)l_x(t)\right]}{\left[l_x^2(t) - l_x(t_o)l_y(t_o)\right]^2} 2l_x(t)$$

Therefore the sign of $\dfrac{df}{dl_x(t)}$ evaluated near the critical point will determine the stability of the critical point. If we simply attempt to substitute the critical point into the expression above we see that the function is 0/0, undetermined. Therefore, we can use L'Hopital's rule to evaluate the limit.

$$\lim_{t\to\infty}\frac{df}{dl_x(t)} = \frac{-\frac{1}{\tau}\left[3l_x(t) - 2\sqrt{l_x(t_o)l_y(t_o)}\right]}{l_x(t)} - \frac{-\frac{1}{\tau}\left[2l_x^2(t) - 3l_x(t)\sqrt{l_x(t_o)l_y(t_o)} + l_x(t_o)l_y(t_o)\right]}{\left[l_x^2(t) - l_x(t_o)l_y(t_o)\right]}$$

We can evaluate the first term at the critical point,

$$\lim_{t\to\infty}\frac{df}{dl_x(t)} = -\frac{1}{\tau} - \frac{-\frac{1}{\tau}\left[2l_x^2(t) - 3l_x(t)\sqrt{l_x(t_o)l_y(t_o)} + l_x(t_o)l_y(t_o)\right]}{\left[l_x^2(t) - l_x(t_o)l_y(t_o)\right]}$$

But the second term is still undetermined. We use L'Hopital's rule again on the second term

$$\lim_{t\to\infty}\frac{df}{dl_x(t)} = -\frac{1}{\tau} - \frac{-\frac{1}{\tau}\left[4l_x(t) - 3\sqrt{l_x(t_o)l_y(t_o)}\right]}{2l_x(t)}$$

If we evaluate it at the critical point, we have

$$\lim_{t \to \infty} \frac{df}{dl_x(t)} = -\frac{1}{\tau} + \frac{1}{2}\frac{1}{\tau} = -\frac{1}{2}\frac{1}{\tau}$$

Since, τ is a relaxation time and is always positive, this term is always negative and the critical point is always stable. There is no complex component, so at least locally, the critical point behaves like a stable node.