Effect of Convection on a Propagating Front with a Solid Product: Comparison of Theory and Experiments

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We studied ascending fronts of acrylamide polymerization in dimethyl sulfoxide in which the reactants in solution are converted to a gel at a higher temperature than the solution. We have calculated the stability boundary (the critical viscosity at which convection occurs) as a function of the front velocity. We found that in a two-dimensional system the presence of walls does stabilize the front compared to an infinite plane, but the shape of the boundary is not affected. Experimental fronts exhibited antisymmetric convection for low viscosities and low front velocities, as predicted by our calculations. However, the experimentally determined boundary differed significantly from the calculated ones, the experimental fronts being more stable. The shapes of the boundaries differ, and we propose this is caused by the temperature dependence of the viscosity, which is not treated in our analysis.

Introduction

Many autocatalytic reactions in solution can sustain a localized reaction front that propagates through an unstirred medium.¹ As a front propagates, concentration and thermal gradients are formed that alter the density of the solution, often causing convection. A great deal of work has been done on fronts that propagate in solution via the coupling of mass diffusion with the autocatalytic polynomial reaction kinetics, both experimentally²⁻²⁰ and theoretically.²¹⁻²⁸

An extensive body of work has been done on the onset of convection in fronts propagating in vertical orientations in which the stability of the system with respect to the onset of convective fluid flow is essentially independent of the front velocity, and the driving force is the change in composition and not the change in temperature. Pojman et al. considered the problem of the onset of simple convection for ascending fronts with liquid products in terms of the Rayleigh number for the static problem.¹⁰,²¹ Masere et al. performed a similar analysis and found good agreement with results for the iodate—arsenous acid system for the onset of antisymmetric convection.⁴ Numerous other works considered various aspects of the problem.²³⁻²⁷,²⁹

Some experimental work has been done on convection that can occur in descending thermal fronts in which a liquid monomer is converted to a solid polymer product.³⁰,³¹ In this work we consider the problem of an ascending thermal front with a liquid reactant that is converted to a solid product. The heat released by the chemical reaction can cause the fluid above the front to flow through the interaction of buoyancy, similarly to the Rayleigh–Bénard problem with heating from below.³² Unlike that situation, the lower boundary is moving (Figure 1). We note that this problem differs from directional solidification in which the low temperature occurs at the solid/liquid interface and the bulk liquid is at the high temperature.³³ Thus the velocity of the front affects the stability of the fluid layer. The

Figure 1. Diagrams of model systems to be studied. A fluid at $T_i$ is converted to a solid product at a final temperature $T_f$ through a propagating front with velocity $c$. (a) The layer is infinite, and dashed lines indicate length corresponding to the tube diameter of the experimental systems. (b) A two-dimensional system with the walls. The precise nature of the interaction between the front and the fluid is the subject of our work.

Frontal Polymerization

Most polymerization reactions are exothermic, and under some conditions, localized zones of reaction can propagate through an unstirred system in a process called frontal polymerization. Chechilo et al. were the first to study frontal polymerization.³⁴ They studied methyl methacrylate polymerization in which the liquid monomer was converted to a solid product. Pojman et al. demonstrated the feasibility of traveling fronts in solutions of thermal free-radical initiators in a variety of neat monomers at ambient pressure using liquid monomers that form polymers with melting points exceeding the reaction temperature of the front.³⁵⁻³⁷ The field was reviewed in 1984 by Davtyan et al.³⁸ and recently by Pojman et al.³⁹ Khan and
Pojman have considered the prospects for frontal polymerization in materials synthesis.\textsuperscript{50}

We set out to study the stability of ascending fronts of polymerization because convective instabilities pose a significant interference to frontal polymerization and because such fronts are good experimental systems for elucidating the role of convection in thermal fronts. We considered two-dimensional models with and without walls and compared the results with experimental data from test tubes.

**Model and Equations**

We make the following assumptions in the mathematical formulation of the problem: (1) The reagents are in a cylindrical tube, whose axis is along the gravitational force. The tube is long, and its radius is large enough that we can neglect the walls. We treat the system as an infinite plane. (We will relax this assumption later by including walls.) (2) The chemical reaction is a one-step zero-order reaction. The reaction rate is then given by an expression of this form:

\[ W = k(T) \varphi(\alpha) \]  

(1)

where \( T \) is the temperature, \( \alpha \) is the degree of conversion, and

\[ \varphi(\alpha) = \begin{cases} 1 & \text{if } \alpha < 1 \\ 0 & \text{if } \alpha = 1 \end{cases} \]

(2)

The temperature dependence of the reaction rate is given by the Arrhenius dependence,

\[ k(T) = k_0 \exp(-E/RT) \]

(3)

where \( E \) is the activation energy, \( R \) the ideal gas constant, and \( k_0 \) the pre-exponential factor. For the asymptotic analysis we will assume the activation energy is large. (3) The liquid is incompressible. The density of the medium depends on the temperature only, and the change of density is small. (4) The coefficient of mass diffusion is much less than the thermal diffusivity. (5) The reaction product is solid or a gel.

Using these assumptions and the Boussinesq approximation, we have the following system of equations for a two-dimensional plane:

\[ \frac{\partial \alpha}{\partial t} = -\nu \nabla \alpha + k(T) \varphi(\alpha) \]

(4)

\[ \frac{\partial T}{\partial t} = -\nu \nabla^2 T + \kappa \Delta T + qk(T) \varphi(\alpha) \]

(5)

\[ \frac{\partial \nu}{\partial t} = -(\nu \nabla) \nu + \nu \Delta \nu + \frac{1}{\rho} \nabla p + g\beta(T - T_0) \gamma \]

(6)

\[ \text{div} \nu = 0 \]

(7)

Here \( \nu = (\nu_x, \nu_y) \) is the velocity of the medium, \( p \) is the pressure, \( \kappa \) is the coefficient of thermal diffusivity, \( q \) is the temperature change caused by the reaction \((T_f - T_0)\), \( \rho \) is the average value of the density, \( \nu \) is the kinematic viscosity, \( g \) is the gravitational acceleration, \( \beta \) is the coefficient of thermal expansion, \( \gamma \) is the unit vector in the z-direction (upward), and

\[ \nabla = \left( \frac{\partial}{\partial x}, \frac{\partial}{\partial y} \right), \quad \Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \]

Equations 4–7 describe the heat diffusion, chemical reaction, and the motion of an incompressible fluid. The heat released by the reaction leads to a temperature gradient that can cause a convective instability.

![Figure 2. Critical frontal Rayleigh calculated as a function of the wavenumber for an infinite layer with Pr = 10.](image)

If we consider a medium at rest, \( \nu = 0 \), the system of two equations (4) and (5) describes condensed phase combustion\textsuperscript{41} and captures many of the essential aspects of frontal polymerization.\textsuperscript{39} The velocity, \( \nu \), of the stationary front and the temperature distribution can be found by an asymptotic analysis for large Zeldovich numbers.\textsuperscript{42}

\[ Z = qE/RT_1^2 \]

(8)

The velocity can be approximated by an equation derived by Novozhilov.\textsuperscript{43}

\[ c^2 = \frac{2k\kappa RT_1^2}{qE} \exp\left(-\frac{E}{RT_1}\right) \]

(9)

A frontal Rayleigh number that determines whether the front is stable can be defined to account for the effect of the front velocity:\textsuperscript{44,45}

\[ Ra = g\beta q/\nu c^3 \]

(10)

It is related to the traditional Rayleigh number for the stability of an infinitely wide fluid layer heated from below by substituting for \( L \) the width of the preheat zone, \( L = \kappa c^{-1} \):

\[ Ra = g\beta qL^3/\nu k \]

(11)

Garbey et al. performed the linear stability analysis for this system in an infinite plane.\textsuperscript{45} We will not provide the details of the analysis but only explain how we have applied it to a real system. The velocity was scaled by dividing by the value obtained from the infinitely narrow reaction zone approximation with the Novozhilov equation. They calculated the critical frontal Rayleigh number as a function of the Prandtl number \((Pr = \nu/\kappa)\) and the dimensionless wavenumber, \( k \),

\[ k = 2\pi/\lambda \]

(12)

where

\[ \lambda = lc/\kappa \]

(13)

and \( c \) is the dimensional velocity of the front, \( l \) is the width of the convective roll, and \( \kappa \) is the thermal diffusivity (see Figure 2). They found that for Prandtl numbers greater than 2, the critical frontal Rayleigh number was only weakly dependent on \( Pr \). Therefore, \( Pr \) was fixed at 10. Although the frontal Rayleigh number is only calculated at one dimensionless velocity, the experimental velocity enters through the calculation of the wavenumber.

To prepare a neutral stability boundary, i.e., the curve in the viscosity–velocity plane that demarcates stable and unstable regions of front propagation, the wavenumber of the perturbation...
was calculated from $l$, which was set equal to the tube diameter. Substituting the relationship between $Ra$, and $k$ fit from Figure 2 into the expression for the critical frontal Rayleigh number, we obtain the following relationship between the critical viscosity and the critical velocity:

$$v_c = \frac{g\beta qk^2}{5c^3 + 40(2\pi x/D)^2c}$$

(14)

### Model with the Effect of Walls

To determine the effect of walls on the stability, we analyzed the same system of equations (4–7) for a bounded two-dimensional plane. (The details of the analysis are presented in the Appendix.) The scaling of the physical width, $L$, is accomplished by

$$L = cl/2\kappa$$

(15)

Figure 3 shows the critical Rayleigh numbers calculated as a function of the scaled velocity for a dimensionless width of 2 ($L = 1$) and a Prandtl number of 10 (again the critical frontal Rayleigh number is insensitive to changes of $Pr$ above $Pr = 2$). Notice how close the values are for the two modes, which are depicted in Figure 4.

To calculate the critical frontal Rayleigh for different dimensional velocities, we calculate $L$ using eq 15 and calculate the dimensionless velocity $\tilde{u}$ by

$$\tilde{u} = L\sqrt{2}$$

(16)

Using this $\tilde{u}$, we calculate the critical frontal Rayleigh number, $Ra$, from the graph in Figure 3 and substitute into eq 10 to obtain

$$v_c = g\beta qk^2(L/\tilde{u})^3 \frac{1}{Ra}$$

(17)

For the case with walls we calculated the streamline functions for the first two modes, shown in Figure 4. The first mode to appear is an antisymmetric fluid motion, and the second is axisymmetric, the same as observed in a nonreacting fluid.

### Choice of the Experimental System

We have assumed that the only change in density occurs from thermal expansion. Because there are significant isothermal density changes in polymerization reactions (as large as 25%), fronts with liquid polymers disintegrate due to the Rayleigh–Taylor instability. Thus, they are not suitable candidates for studying simple convective instabilities.

Fronts that produce solid products, such as methacrylic acid and triethylene glycol dimethacrylate, could be studied. However, bubbles that are formed from by-products of the initiators interfere with ascending fronts. The bubbles rise from the front, causing fluid motion that obscures any convection caused by the front itself. Bubbles can be suppressed by performing the fronts in a pressure reactor, but this is difficult.

Fronts of epoxy curing can be used (with BCl₃–amine complex as the curing agent), but the epoxy resin’s viscosity can change by 2 orders of magnitude from the initial to the front temperature, and the velocity can only be varied from 0.5 to 1 cm/min. At higher concentrations of the BCl₃–amine complex the formation of bubbles prevents reliable front velocity measurements.

Pojman et al. recently developed an ideal system that is bubble-free. Fronts with acrylamide (and a small amount of bisacrylamide to cross-link the product and prevent fingering) dissolved in dimethyl sulfoxide (DMSO) with potassium persulfate as the initiator are excellent for studying convection because there are no bubbles and the front velocity can be varied from 0.5 to 2.5 cm/min.

### Comparison of Assumptions of the Model with the Physical System

1. The reaction zone is infinitely narrow; that is, the concentration profile of the product is a step function. Figure 5 shows a temperature profile of a convection-free front. Because gelation occurs at much less than complete conversion, the maximum temperature (167 °C) occurs not at the solid–liquid interface but rather 2 mm behind the gel point. Because no convection can occur in the gelled medium, we used the temperature at the interface (75 °C) to calculate the $q$ in our calculations.

2. The viscosity is independent of temperature. The viscosity of the medium is certainly a function of temperature, as seen in Figure 6, varying as much as a factor of 20 from 25 to 75 °C. We used the viscosities measured at the interface temperature and the initial temperature in our comparisons.

3. The thermal diffusivity is independent of temperature and conversion. This appears to be a reasonable assumption, as we will see below, where we calculate the $\kappa$ from the temperature profile.

### Experimental Section

All chemicals were used as received: potassium persulfate, N,N-methylenbisacrylamide, and acrylamide (99%) from Aldrich; dimethyl sulfoxide from Fisher; and Cab-O-Sil amorphous fumed silica from Cabot Corporation.

#### Stability and Velocity Measurements

The system consisted of acrylamide dissolved in dimethyl sulfoxide (DMSO). The initiator, potassium persulfate, was used along with hydroquinone to inhibit homogeneous polymerization and N,N-methylenbisacrylamide to cross-link the polymer. The concentration of acrylamide was 1:1 w/v. The N,N-methylenbisacrylamide concentration was 1% w/v of the total solution. The amount of hydroquinone used was 0.10 g for every 64 mL of DMSO. Such a small amount of hydroquinone was used because higher hydroquinone concentrations affect the velocity of the front. The amount of initiator used was varied in order to change the velocity of the front. The concentration was usually between 0.5% and 2.5% of solution.

Amorphous fumed silica (Cab-O-Sil) was added to vary the viscosity of the system. The amount used ranged between 2% and 3% of the solution. Once the Cab-O-Sil was added, the mixture had to be briefly degassed in order to properly mix the Cab-O-Sil with the solution. The mixture was placed in a 16 × 150 mm borosilicate culture tube (Fisher). For reasons we...
do not know, the Cab-O-Sil increased the rate of homogenous polymerization, i.e., reduced the pot life.

Initially, heat was applied to the mixture to start the front with a soldering iron in contact with the solution or through the glass. For an ascending front, some solution without Cab-O-Sil was added to a small amount of 400 µm Glas-Shot (Cataphote) in the bottom of the tube. The mixture with Cab-O-Sil was added on top of this. The front was first ignited in the Glas-Shot mixture. This allowed the Cab-O-Sil mixture front to be ignited by the flat surface of the Glas-Shot front. After the front was initiated, the tube was inserted into a side-armed 250 mL Erlenmeyer flask with a rubber gasket and evacuated. This procedure was done in order to eliminate external convection of the air surrounding the tube. Each ascending and descending front was videotaped with a Cohu High Performance CCD camera.

**Viscosity Measurements.** To measure the viscosity of the mixtures, Cannon-Fenske routine viscometers were used. For the Cab-O-Sil 2% mixture, a size 200 Cannon-Fenske viscometer was used. For all of the other mixtures a size 300 viscometer was used. These viscometers were not necessarily used for their designated viscosity range but for their capillary size. The Cab-O-Sil tended to block the viscometers with smaller capillaries. To determine if using a viscometer that was out of the viscosity range of the liquid made a large difference in the measurement, the viscosity of pure dimethyl sulfoxide was measured using the size 200 Cannon-Fenske viscometer. The viscosity measurement had a 4.5% difference from the accepted value of dimethyl sulfoxide viscosity.

To measure viscosity, the viscometer was charged with the mixture. The viscometer was then placed in a water bath of 75 °C and allowed to equilibrate for 15 min. A stopwatch was then used to measure the time needed for the liquid to move through the capillary. Three time measurements were recorded for each mixture. These measurements were averaged, and this time was multiplied by the viscometer constant provided by the manufacturer at 75 °C. (The gel point of the front is 80 °C, but it was difficult to maintain our water bath above 75 °C.) We ignored this small effect on the viscosity. The preceding procedure was also followed to obtain the viscosities at 40 and 25 °C.

**Front Temperature, Density, and Thermal Expansion Coefficient Measurements.** The temperature of the front was obtained using an unsheathed Omega thermocouple (6 in., part TMQSS-020G-6). This thermocouple was formed into a spiral parallel with the front and placed in a test tube containing the mixture. The thermocouple was attached to an Omega thermocouple thermometer. The run was videotaped in order to observe the location of the front and the thermometer display simultaneously. This was done three times, and the average gel point was found to be 75 ± 5 °C.

It was determined that the mixture without Cab-O-Sil has a density of 1.18 g cm⁻³ at 25 °C. The density was again measured as a function of temperature in order to determine the thermal expansion coefficient. For these measurements, a 50 mL pycnometer and a water bath were used. At room temperature, the pycnometer was filled with the solution and weighed. The pycnometer with solution was then heated, and the solution was allowed to overflow as it expanded. When the next desired temperature was reached, the pycnometer and solution were reweighed. This procedure was followed for four
temperatures. Then the density at each temperature was calculated to be 1.18 g/cm³ at 25 °C; 1.16 g/cm³ at 42 °C; 1.15 g/cm³ at 62 °C; and 1.13 g/cm³ at 75 °C. To determine the thermal expansion coefficient, the collected data and the following equation were used:

$$\beta = \frac{\Delta V/V_i}{\Delta T}$$  \hspace{1cm} (18)

where $\beta$ is the thermal expansion coefficient, $V_i$ is the initial volume, $\Delta V$ is the change in volume, and $\Delta T$ is the change in temperature. A thermal expansion coefficient value was calculated for each of the three changes in temperature. The thermal expansion coefficient is $9.9 \times 10^{-4}$ °C⁻¹.

Criteria for Determining Stability. Unstable ascending fronts propagate faster than stable ones. Thus, it should be possible to compare the velocity of an ascending and descending front with the same viscosity to determine the stability. However, near the stability boundary the velocities are nearly identical (within a few percent). Therefore, we injected a drop of bromophenol/DMSO solution above the front. If the blue solution moved as the front propagated upward, the front was counted as unstable.

Determination of the Thermal Diffusivity. We estimated the thermal diffusivity of the acrylamide/DMSO/Cab-O-Sil mixture from the temperature profile from the relationship between the front velocity ($c$), temperature profile, and thermal diffusivity:

$$T(x) = T_0 + \Delta T \exp\left(c x / \kappa \right)$$  \hspace{1cm} (19)

Figure 7 shows the fit that provides a value for $\kappa = 0.06$ cm² min⁻¹ (1 × 10⁻⁴ cm² s⁻¹).

Results

Descending fronts are always flat, but the shapes of ascending fronts depend on the velocity and viscosity. If the viscosity and/or velocity are large enough, the ascending front is flat. If we fix the velocity at 2.6 cm/min and decrease the viscosity, at a critical value (0.04 cm² s⁻¹) the ascending front will become slightly distorted, as seen in Figure 8. The fluid above the front moves in an antisymmetric roll. The front velocity is only a few percent faster than the descending front, but the fluid velocity in the convective roll can be significant (on the order of 1 cm/min). This corresponds to the streamlines shown in Figure 4a.

As the viscosity is decreased further (0.025 cm² s⁻¹), a new mode of convection occurs. Figure 9 shows an axisymmetric front that propagates much faster than its descending version (2.63 cm/min versus 6.11 cm/min). This corresponds to the streamlines shown in Figure 4b. This sequence of convective modes is the same as observed in ascending fronts in the iodate-arsenous acid system.

By analyzing the behavior of 33 ascending fronts, we determined a stability boundary, which is shown in Figure 10. We have estimated the exact position of the boundary between fronts that were stable and the next one at the same viscosity but a different velocity. For the two highest viscosities it was not possible to have a slower front without homogeneous reaction. Thus, we can only say for those viscosities that the boundary cannot occur at higher front velocities. The results are shown for the viscosities measured at 75 °C. Although we did not map out the complete boundary between the antisymmetric mode and the axisymmetric one, the one point we measured is consistent with the stability analysis in that the axisymmetric mode is quite close to the boundary between a planar and antisymmetrically shaped front.

Figure 11 shows a comparison of the experimental boundaries (using viscosities at 26 and 75 °C) with those calculated for an infinite plane and a bounded plane.
Effect of Convection on a Propagating Front

It is interesting to see that the inclusion of walls in the calculation does stabilize the front but does not change the dependence of the critical viscosity on the velocity. Also, the critical viscosity dependence on the velocity is not just to \(c^{-3}\), as might be expected from the frontal Rayleigh number in eq 10, but shows the dependence of the form in eq 21. This is because the critical frontal Rayleigh number is itself a function of the velocity.

The experimentally determined stability boundary in Figure 10 differs from both calculated ones in two ways. The experimental boundary is lower in the plane than the calculated boundaries, which means the experimental fronts are more stable than predicted. Errors in the determination of \(q, \beta, \text{ or } \kappa\) would cause a shift in the boundary along the \(y\)-axis without changing the dependence of the critical viscosity on the front velocity. More important is the difference in functional dependence of the boundary. Both the calculated boundaries have the form of eq 21, but the experimental one shows a weaker dependence on the velocity.

We consider several possible reasons why the calculated boundary does not agree with the experimental data.

1. The \(\Delta T\) is a function of the front velocity. We measured the temperature profile for a front with 0.89 cm/min velocity. The overall temperature change is lower than that for the 1.7 cm/min front, but the temperature at which the gel forms is still 75 °C.

2. There is a systematic error in viscosity measurements. The fluid is non-Newtonian and probably is a Bingham plastic at high concentrations, meaning it possesses an infinite viscosity up to a critical shear.\(^{49}\) However, at the low Cab-O-Sil concentrations used, the fluid flows readily. The fluid flows observed in the viscometer were on the same order as those observed in the convective rolls (about 1 cm/min).

3. The thermal diffusivity, \(\kappa\), is a function of \(T\) and/or conversion. However, we successfully fit the temperature profile to obtain \(\kappa\).

4. The viscosity is temperature dependent. We believe that this is the most significant cause for the deviation of the calculated boundary from experimental ones. Future work should include this effect and a calculation and experimental determination of the boundary between the two modes.

Conclusions

We have calculated the stability boundary (the critical viscosity at which an ascending front becomes unstable) as a function of the front velocity. We found that in a plane the presence of walls does stabilize the front compared to an infinite plane, but the shape of the boundary is not affected. The experimentally determined boundaries differ significantly from the calculated ones, the experimental fronts being more stable, but the qualitative trend is the same. The difference between the boundaries could be caused by uncertainty in the constants used in the calculations. The shapes of the boundaries differ, and we propose this is caused by the temperature dependence of the viscosity, which is not treated in our analysis.

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Appendix: Linear Stability Analysis of System with Walls

Following the linear stability analysis\(^{45}\) of the system (4)-(7), we consider the eigenvalue problem for the streamline function \(\psi\) and the dimensionless temperature \(\theta\): \(^{(A.1)}\)

\[
\begin{align*}
Pr\Delta\psi + \frac{\partial}{\partial z} \Delta \psi - \omega \Delta \psi + Q \frac{\partial \theta}{\partial x} &= 0 \\
\Delta \theta + \frac{\partial}{\partial z} \Delta \theta - \omega \theta - \partial_{\xi}(\zeta \partial_{\xi} \psi)^{x} &= 0 \\
-1 &\leq x \leq 1, z \geq 0
\end{align*}
\]

with boundary conditions \(^{(A.2)}\)

\[
\begin{align*}
x &= -1, 1; & z &= 0, \infty; & \frac{\partial \psi}{\partial x} &= 0 \\
\frac{\partial \theta}{\partial z} &= 0 \\
\frac{\partial \theta}{\partial z} &= -u \theta & z &= \infty; & \theta &= 0
\end{align*}
\]

where prime denotes the derivative with respect to the \(z\)-coordinate, \(Pr\) is the Prandtl number:

\[
Pr = \nu / \kappa
\]

and \(Ra\) is the frontal Rayleigh number:

\[
Ra = \frac{c}{\kappa} \sqrt{\beta q k^{2} / v c^{3}}
\]

Here, \(c\) is dimensional front velocity, and \(u\) is the dimensionless front velocity. The solution is found in the following form:

\[
\begin{align*}
\psi(x, z) &= \sum_{j=0}^{\infty} \phi_{j}(x) a_{j}(z) \\
\theta(x, z) &= \sum_{j=0}^{\infty} \tau_{j}(x) b_{j}(z)
\end{align*}
\]

with the conditions \(^{(A.5)}\)

\[
\begin{align*}
a_{j}(0) &= a'_{j}(0) = 0
\end{align*}
\]

\[
\begin{align*}
b_{j}(0) + \mu b_{j}(0) &= 0
\end{align*}
\]

Here \(\phi_{j}\) and \(\tau_{j}\) are the eigenfunctions of the corresponding operators in the section of a cylinder: \(\phi_{j}(x)\) are the eigenfunctions of the problem

\[
\tilde{\Delta}^{2} \phi + \lambda \tilde{\Delta} \phi = 0 \quad (A.6)
\]

\[
\phi(\pm 1) = \phi'(\pm 1) = 0 \quad (A.7)
\]

The even eigenfunctions are

\[
\phi_{j}(x) = \frac{1}{\sqrt{I_{j}}} \left[ \frac{\cosh k_{j} - \lambda_{j}}{\cos k_{j}} \right] i = 0, 2, 4, \ldots \quad (A.8)
\]

\[
I_{j} = \frac{\lambda_{j}}{2(k_{j}^{2} - \lambda_{j})} \quad (A.9)
\]

and the odd eigenfunctions are

\[
\phi_{j}(x) = \frac{1}{\sqrt{I_{j}}} \left[ \frac{\sinh k_{j} - \lambda_{j}}{\sin k_{j}} \right] i = 1, 3, 5, \ldots \quad (A.10)
\]

Here

\[
\begin{align*}
I_{j} &= \frac{\lambda_{j}}{2(k_{j}^{2} - \lambda_{j})} \quad (A.11)
\end{align*}
\]

The even eigenvalues are

\[
\sqrt{\lambda_{j} - k^{2}} \tan \sqrt{\lambda_{j} - k^{2}} = -k \tanh k \quad (A.12)
\]

and \(k\) is the wavenumber in the \(y\)-direction. Now, \(\tau_{j}(x)\) are the eigenfunctions of the problem:

\[
\tau'' + \mu \tau = 0 \quad (A.13)
\]

\[
\tau(\pm 1) = 0 \quad (A.14)
\]

The even eigenfunctions are

\[
\tau_{j}(x) = \cos \frac{\pi x}{2} i \quad i = 0, 2, 4, \ldots \quad (A.15)
\]

and the odd eigenfunctions are

\[
\tau_{j}(x) = \sin \frac{\pi x}{2} i \quad i = 1, 3, 5, \ldots \quad (A.16)
\]

The odd eigenvalues are

\[
\sqrt{\mu_{j} - \mu} = \pi i / 2 \quad (A.17)
\]

and

\[
\int_{-1}^{1} \tau_{j} \ dx = 0 \quad i \neq k \quad (A.18)
\]

Then the equations for the streamlines and the temperature take the form

\[
Pr(a''_{j} - 2\lambda_{j}a''_{j} + \lambda_{j}^{2}a_{j}) + u(a''_{j} - \lambda a_{j}) - \omega(a''_{j} - \lambda a_{j}) - Q \sum_{j=0}^{\infty} \sigma_{j} b_{j}(z) = 0 \quad (A.19)
\]

\[
b_{j}'' + (\mu_{j} + \omega) b_{j} + \frac{u}{\mu_{j}} e^{-uc} \sum_{j=0}^{\infty} \sigma_{j} a_{j}(z) = 0 \quad (A.20)
\]

We limit our stability analysis to the first term of the infinite sum by \(j\). We also take \(\omega = 0\). It corresponds to the cellular instability where the front is curved, but its shape as well as the whole convective structure does not depend on time. (Periodic in time or pulsating instability appears if \(\omega\) is imaginary.) In this case the eigenvalue problem (A.1) takes the form

\[
\sqrt{\lambda_{j} - k^{2}} \tan \sqrt{\lambda_{j} - k^{2}} = -k \tanh k \quad (A.12)
\]
Let us denote the particular solutions corresponding to the cases

First case:

\[ \tau_1 = -\frac{u}{2} - \sqrt{\frac{u^2}{4} + \mu}, \quad \tau_j = \tau_{j-1} - u, \quad j = 2, 3, \ldots \]

\[ m_1 = 1 \]

\[ m_j = \frac{-u}{\mu \sigma_j k_{j-1}} \quad \tau_j^2 + u\tau_j - \mu, \quad j = 2, 3, \ldots \]

\[ k_j = \frac{Q\sigma_m j}{(\tau_j^2 - \lambda)(Pr\tau_j^2 + u\tau_j - Pr\lambda)}, \quad j = 1, 2, \ldots \]

Second case:

\[ \tau_1 = -\sqrt{\lambda}, \quad \tau_j = \tau_{j-1} - u, \quad j = 2, 3, \ldots \]

\[ m_1 = 0 \]

\[ m_j = \frac{-u}{\mu \sigma_j k_{j-1}} \quad \tau_j^2 + u\tau_j - \mu, \quad j = 2, 3, \ldots \]

\[ k_j = \frac{Q\sigma_m j}{(\tau_j^2 - \lambda)(Pr\tau_j^2 + u\tau_j - Pr\lambda)}, \quad j = 1, 2, \ldots \]

Third case:

\[ \tau_1 = -\frac{u}{2Pr} - \sqrt{\frac{u^2}{4Pr^2} + \lambda}, \quad \tau_j = \tau_{j-1} - u, \quad j = 2, 3, \ldots \]

\[ m_1 = 0 \]

\[ m_j = \frac{-u}{\mu \sigma_j k_{j-1}} \quad \tau_j^2 + u\tau_j - \mu, \quad j = 2, 3, \ldots \]

\[ k_j = \frac{Q\sigma_m j}{(\tau_j^2 - \lambda)(Pr\tau_j^2 + u\tau_j - Pr\lambda)}, \quad j = 1, 2, \ldots \]

Let us denote the particular solutions corresponding to the cases

\[ \tau_1 = -\frac{u}{2} - \sqrt{\frac{u^2}{4} + \mu}, \quad \tau_j = \tau_{j-1} - u, \quad j = 2, 3, \ldots \]

\[ m_1 = 1 \]

\[ m_j = \frac{-u}{\mu \sigma_j k_{j-1}} \quad \tau_j^2 + u\tau_j - \mu, \quad j = 2, 3, \ldots \]

\[ k_j = \frac{Q\sigma_m j}{(\tau_j^2 - \lambda)(Pr\tau_j^2 + u\tau_j - Pr\lambda)}, \quad j = 1, 2, \ldots \]

and the boundary conditions are

\[ V(0) = V'(0) = 0, \quad \Theta'(0) + u\Theta(0) = 0 \]

Then the linear system of equations results in

\[ \begin{pmatrix} c_1\varphi_1(0) + c_2\varphi_2(0) + c_3\varphi_3(0) = 0 \\
 c_1\varphi_1'(0) + c_2\varphi_2'(0) + c_3\varphi_3'(0) = 0 \\
 c_1(\varphi_1'(0) + u\varphi_1(0)) + c_2(\varphi_2'(0) + u\varphi_2(0)) + c_3(\varphi_3'(0) + u\varphi_3(0)) = 0 \end{pmatrix} \]

and the condition

\[ \begin{vmatrix} \varphi_1'(0) & \varphi_2'(0) & \varphi_3'(0) \\
 \varphi_1(0) & \varphi_2(0) & \varphi_3(0) \\
 \varphi_1'(0) + u\varphi_1(0) & \varphi_2'(0) + u\varphi_2(0) & \varphi_3'(0) + u\varphi_3(0) \end{vmatrix} = 0 \]

gives the critical Rayleigh number corresponding to the stability boundary.

**Numerical Methods**

Equation A.32 with expressions A.25–A.28 was solved for different parameter values of \( Pr \) and \( u \) resulting in critical Rayleigh numbers \( Ra_c \). The solution algorithm involved the calculation of the determinant (A.32) for a set of \( Ra \) values (for example, from 0 to \( 10^6 \)), and when the sign of the determinant changed, the exact solution was found in the interval by consecutively dividing the \( Ra \) step by half until a given precision of the root was reached. If more than one root was found, the lowest value of \( Ra \) was considered to be the critical Rayleigh number. Sometimes the singular solutions were found (i.e., the determinant (A.32) changed sign through infinity). These solutions were excluded from our consideration.

**Results and Discussion**

As follows from the linear stability analysis for the first unstable mode, the following values of constants are be taken:

\[ \sigma_1 = \sigma_2 = -\frac{\pi^2}{3}, \quad \mu = \frac{\pi^2}{4}, \quad \lambda = \frac{\pi^2}{\lambda} \]

While for the second unstable mode we used the following values:

\[ \sigma_1 = \sigma_2 = -2\pi^2/\lambda(\lambda - \pi^2), \quad \mu = \frac{\pi^2}{\lambda} \]

and the first positive root of the equation \( \tan(\sqrt{\lambda}) = \sqrt{\lambda} \) for \( \lambda \). When \( Ra \) critical was calculated for a series of Prandtl numbers \( Pr \) using constants from (A.33) and (A.34), we compared the stability of both modes. Lower critical Rayleigh numbers for the first mode mean this instability appears first as we increase the Rayleigh number by decreasing the initial solution viscosity or the front velocity (see Figure 2). To calculate the eigenfunctions corresponding to zero eigenvalue (critical frontal Rayleigh number), we used the following formulas:

\[ \psi(x,z) = \psi(z)(1 + \cos(\pi z))/\pi \]

\[ \vartheta(x,z) = \vartheta(z) \sin(\pi z/2) \]

The first component here is the stream function \( \psi \), and the second one is the dimensionless temperature \( \vartheta \). The level lines of the stream function give the lines along which the liquid moves. Figure 4 shows the streamlines of the fluid motion and corresponding temperature fields for both calculated modes.
These pictures exactly match the experimental observations of convection in ascending polymerization fronts.

References and Notes