

Polymer Crystallization Waves

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SUMMARY. - *We prove the existence of travelling wave solutions for a polymer crystallization model. The mathematical problem governing the process consists in a system of two coupled first order PDE, the heat equation with a source term for the temperature and the isokinetic law, involving an order parameter $\psi \in [0, 1]$, whose extreme values correspond to pure phases.*

1. Introduction

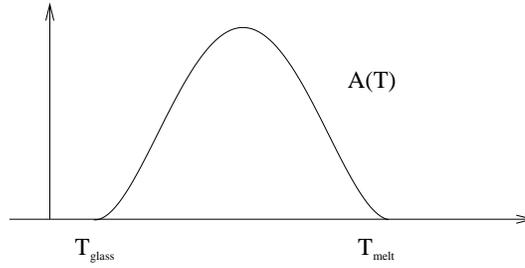
Crystallization of polymers is a complex process in which the long chain of the polymer macromolecules rearrange into a more regular and less energetic quasi-crystall structure.

For low temperature the polymer chains are entangled and there is not enough energy to allow for the chains to rearrange further. This “phase” is generally denoted as “glass”. On the contrary, for high temperature the polymer melts into a liquid phase.

This means that the crystallization takes place in a temperature range (T_{glass}, T_{melt}) and is not a sharp transition like in the Stefan model for phase change.

The complete thermodynamic state of the polymer can be defined by the temperature T and an order parameter $\psi \in [0, 1]$ whose extreme values correspond to “pure” phase, $\psi = 0$ in a completely disordered polymer (typically in the liquid phase) and $\psi = 1$ for a completely ordered polymer or *crystall*.

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Figure 1: Typical form of the function $A(T)$ 

During the crystallization the temperature obeys to a heat equation with a “source” term due to the latent heat released from the polymer fraction changing into the less energetic crystalline phase

$$c\rho\frac{\partial T}{\partial t} - \operatorname{div}(K\nabla T) = \lambda\frac{\partial\psi}{\partial t} \quad (1)$$

where λ is the latent heat of crystallization.

The general form of the kinetic equation for ψ involves the history of the material, but for a large class of problems it can be simply represented by an equation of the form

$$\frac{\partial\psi}{\partial t} = A(T)B(\psi) \quad (2)$$

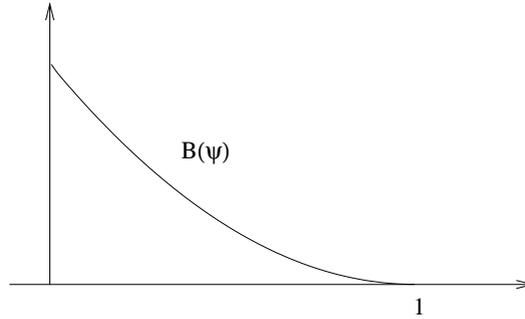
where $A = 0$ for $T \notin (T_{glass}, T_{melt})$ and $B(\psi) = 0$ for $\psi > 1$.

Here we are looking for travelling wave solutions of the system of equations (1), (2).

One can expect this kind of solution in analogy with the case of the heat (diffusion) equation with a non linear source term introduced by Fisher [3] and whose mathematical treatment was first given in the celebrated paper of Kolmogorov, Petrovskiĭ and Piskunov [1]. There the case of the equation

$$u_t - u_{xx} = f(u) \quad (3)$$

was considered, with $f(u) > 0$ for $u \in (0, 1)$, $f'(0) > 0$, $f'(1) < 0$. Then a family of travelling wave exists joining the value 0 and 1 at infinity.

Figure 2: Typical form of the function $B(\psi)$ 

In our model we still have a heat equation with a source which is active only in a bounded range of temperature but now the source term depends on an additional unknown function.

A first approach to the problem can be found in [2], where the case of discontinuous reaction term $A(u) = \chi_{(u_{min}, u_{max})}$ was considered. Under this assumption the solution of the travelling wave system can be explicitly computed, and a monotonicity argument was used to deduce the existence of the bounded travelling wave. Moreover the authors construct travelling waves with a front by passing to the limit when the reaction term $A(U)$ tends to a Dirac measure, obtaining the travelling wave solution for the supercooled Stefan problem.

In this paper we are concerned with generic but smooth reactions terms. That makes impossible to compute the solution explicitly and a detailed phase space analysis of the traveling wave system is needed to prove that travelling wave solutions exist, with monotone profiles of both the temperature and the crystalline fraction.

A major difference with the case of equation (3) is that now conditions at infinity are not uniquely defined. This is because conditions at infinity corresponds to the equilibria (T, ψ) of the kinetic equation (2), which is now a large set, made of three relevant subset: the whole *glass* region $\mathcal{G} = \{T \leq T_{min}, 0 \leq \psi \leq 1\}$, the completely crystallized polymer $\mathcal{C} = \{T_{min} \leq T \leq T_{max}, \psi = 1\}$, and the partially converted polymer at the melting temperature

$\mathcal{M} = \{T = T_{max}, 0 \leq \psi \leq 1\}$.

We show that the lower limit must belong to the glass region \mathcal{G} , and can be “arbitrarily” chosen, while the upper limit may belong to both regions \mathcal{C} and \mathcal{M} , depending on the value of the lower limit and of the normalized value of the latent heat.

2. The wave system

Since we are looking for travelling wave type solutions, we first rewrite the equations in dimensionless one-dimensional setting as

$$u_t - u_{xx} = Lw_t \quad (4)$$

$$w_t = A(u)B(w) \quad (5)$$

where we indicate again by $A(u)$ and $B(w)$ the functions in the kinetic law. We assume that $u = 0$ now corresponds to the glass-transition temperature T_{glass} and $u = U_M$ corresponds to the melting temperature T_{melt} .

We define

$$u(x, t) = U(x + at) \quad (6)$$

$$w(x, t) = W(x + at) \quad (7)$$

where a is a constant (the wave speed) to be determined. Then (4), (5) become

$$(U' - aU + aLW)' = 0 \quad (8)$$

$$W' = \frac{1}{a}A(U)B(W) \quad (9)$$

where $(\)'$ denotes the derivative with respect to $\xi = x + at$.

Because of the symmetries of the problem, it can be easily realized that wave solutions are defined up to a *shift* constant, and that the transformation $\xi \rightarrow -\xi$ maps progressive travelling waves ($a < 0$) into regressive ones ($a > 0$) and viceversa. Then, in the following we always assume the wave to be a regressive one ($a > 0$), and we fix the shift assuming $U(0) = 0$.

One more consideration is needed in order to give a correct physical interpretation of our results. The model represented by equations (1) and (2) makes sense only for temperature below the melting

temperature T_{max} , since it does not take into account the melting itself (from equation (2) we deduce that ψ is constant in the region $T > T_{max}$), then we are interested in solutions which satisfy the inequalities $U \leq U_M$ and $0 \leq W \leq 1$.

Since we are looking for bounded monotone travelling waves, we can assume that U' vanishes at infinity. Then equation (8) can be integrated assuming conditions at $-\infty$. We assume that

$$U(-\infty) = U_- < 0, \quad W(-\infty) = W_- \in [0, 1) \quad (10)$$

i.e. we assume that the polymer upstream of the wave is at a temperature in the glass region and is not completely crystallized.

Then system (8)-(9) can be written as a first order system

$$U' = a[U - LW - U_- + LW_-] \quad (11)$$

$$W' = \frac{1}{a}A(U)B(W). \quad (12)$$

We state the following

THEOREM 2.1. *For any $L > 0$ and for any $U_- < 0$ and $W_- \in [0, 1)$, with $\frac{1-W_-}{-U_-} < \frac{1}{L}$, there exists a unique, modulo space shift, regressive travelling wave $(U(\xi), W(\xi))$ such that $U(-\infty) = U_-$, $W(-\infty) = W_-$.*

If $L > \frac{U_M - U_-}{1 - W_-}$, then $U(+\infty) = U_M$ and $W(+\infty) < 1$. i.e. we have a partial crystallization. If $L < \frac{U_M - U_-}{1 - W_-}$, then $U(+\infty) < U_M$ and $W(+\infty) = 1$. i.e. we have a complete crystallization.

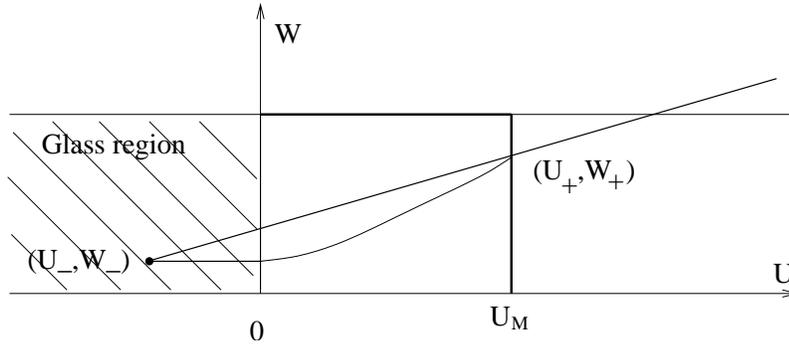
The proof of the theorem is the object of next Sections.

Let us remark that equilibria for (11)-(12) are the intersections of the straight line r of equation $U - LW = U_- - LW_-$ with the zero set of the function $A(U)B(W)$, which is composed of the region $U \leq 0$ (the glass region), and the two lines $W = 1$ and $U = U_M$ (of course we are interested only on values in the the strip $0 \leq W \leq 1$).

Depending on the different values of U_- , W_- and L , three possible situations arise:

1. the intersection of the line r with the equilibrium zone is completely contained in the glass region \mathcal{G} ;

Figure 3: Equilibria



2. the line r intersects the segment line $0 < U < U_M, W = 1$;
3. the line r intersects the segment line $U = U_M, 0 < W < 1$.

It is immediate to realize that in the first case no travelling waves exist except for the trivial one defined by constant solutions, while in both cases 2 and 3 the traveling wave solution exists, as stated in Theorem (2.1).

The three cases can be interpreted physically, remarking that the slope of the line r is equal to $\frac{1}{L}$.

Accordingly, for very small values of the latent heat or very high values of the fraction of crystallized polymer in the “glass” phase, that is in case 1, it is not possible to connect a downstream and an upstream equilibria with a traveling wave.

Increasing the value of the latent heat we obtain case 2, which corresponds to a wave with downstream temperature in the activation range $(0, U_M)$ of the crystallization dynamics and a complete conversion of the polymer into the crystal phase.

Finally for values of the latent heat larger than the normalized melting temperature, i.e. if L satisfies $L > U_M$, case 3 becomes possible (for appropriate upstream conditions of the temperature and of the fraction of crystallized polymer). In this case the wave solution leads to a “partial” conversion of the polymer with a downstream temperature equal to the melting temperature.

3. Construction of the wave solution

Since W is constant throughout the glass region \mathcal{G} , the system can be easily integrated to obtain

$$W(\xi) = W_-, \quad U(\xi) = U_- \left[1 - e^{a\xi} \right] \quad (13)$$

where we have chosen the *shift* in the wave in order to have $U(0) = 0$, i.e. the solution is in the glass region for any $\xi < 0$. In particular, this means that any wave solution originating from a point of the glass region (for $\xi = -\infty$) enters the reacting region $0 < U < U_M$, $0 \leq W < 1$ at a point below the line $U - LW = U_- - LW_-$ where $U' = 0$.

Suppose now that the line r intersects either the segment line $0 < U < U_M$, $W = 1$ or the segment line $U = U_M$, $0 < W < 1$. In both cases we denote by (U_+, W_+) the intersection point.

To prove the existence of the wave we have to prove that a value of the wave speed a exists such that the solution $(U(\xi), W(\xi))$ of (11) and (12), with initial data $U(0) = 0$ and $W(0) = W_-$, satisfies

$$\lim_{\xi \rightarrow +\infty} (U(\xi), W(\xi)) = (U_+, W_+) \quad (14)$$

Moreover, the positive trajectory (i.e. the trajectory for $\xi > 0$) of this solution must belong to the trapezoidal region \mathcal{T} , defined as the intersection of the rectangle $\{0 < U < U_M, 0 < W < 1\}$ and the half plane $U - LW > U_- - LW_-$, which is the only region in the phase plane where both U' and W' are positive (remember that we don't want the solution to enter the region $U > U_M$.)

Unfortunately \mathcal{T} is not an invariant region. So we have to prove first that there exist solutions with positive trajectory in \mathcal{T} and limit point (U_+, W_+) . Those are the only bounded solutions of our initial value problem, as we'll prove in the next subsection.

We deal first with the linearisable case and then with the zero eigenvalue case: in this case, we limit ourselves to consider the case of partial crystallization, that is with $U_+ = U_M$ and $W_+ < 1$, the proof being analogous in all the cases.

Section 3.3 contains the study of the behaviour of the bounded solutions for different values of the speed a : we prove that there exists exactly one solution for any sufficiently large value of a .

Then we have to prove that there exists one (and only one) value of the speed a such that the corresponding bounded solution originates from our initial conditions. This is done in Section 4 where we conclude the proof of the Theorem using monotonicity and continuity arguments.

3.1. The bounded solution in the linearizable case

We first consider the case of continuous reaction terms $A(U)$ and $B(W)$ which belong to $C^1(0, U_M)$ and $C^1(0, 1)$ respectively but have non vanishing left derivatives at the right boundary,

$$A'(U_M) = a_1 < 0, \quad B'(1) = b_1 < 0. \quad (15)$$

Then, in the original model, the reaction terms are not globally C^1 . However, as we anticipated, the model is only meaningful for $U \leq U_M$ and $W \leq 1$. This makes it possible to redefine the reaction terms for $U > U_m$ and $W > 1$ in such a way that the corresponding new system (11) and (12) has a globally C^1 right hand side. This implies that for $U > U_m$ and $W > 1$ both the extensions of A and B are negative, at least in some neighbourhood of these points. Working with this new smooth reaction terms will make it possible to use linearization techniques, and does not alter the meaning of our results as long as the solution remains in the region $U \leq U_M$ and $W \leq 1$.

In this case the following proposition ensures the existence of the requested bounded solution .

PROPOSITION 3.1. *Under condition (15), if either $W_+ < 1$ or $U_+ < U_M$, there exists a unique solution with positive trajectory in \mathcal{T} and limit point (U_+, W_+) .*

Proof. It is enough to linearize the system around the equilibrium (U_+, W_+) . The corresponding matrix is

$$\begin{pmatrix} a & -aL \\ \frac{1}{a}A'(U_+)B(W_+) & \frac{1}{a}A(U_+)B'(W_+) \end{pmatrix} \quad (16)$$

It is straightforward to verify that in both cases $W_+ < 1$ and $U_+ < U_M$, the matrix has one negative and one positive eigenvalue, i.e. the equilibrium is a saddle point.

The eigenspace corresponding to the negative eigenvalue is defined by the equation

$$\frac{w}{u} = \frac{1}{L} \frac{1}{2} \left[1 + \sqrt{1 - \frac{4La_1B(W_+)}{a^2}} \right] > \frac{1}{L} \quad (17)$$

if $W_+ < 1$, or

$$\frac{w}{u} = \frac{1}{L} \left[1 - \frac{1}{a^2} A(U_+) b_1 \right] > \frac{1}{L} \quad (18)$$

if $U_+ < U_M$, where now we indicate by u and w the coordinates centered at the critical point.

In both cases the eigenspace is a line, which, for values of U approaching U_+ from below, lies in the trapezoidal region \mathcal{T} . This implies that there exists one and only one solution whose trajectory belongs to \mathcal{T} for large enough ξ and with limit (U_+, W_+) . \square

3.2. The bounded solution in the zero eigenvalue case

In the case of C^1 reaction terms, as well as in the case in which the straight line r passes through the point $U = U_M, W = 1$, the linearization produces a matrix with only one non zero eigenvalue. In fact now $a > 0$ is an eigenvalue with associated eigenspace $w = 0$. The second row of the jacobian matrix (16) vanishes, and zero is then the second eigenvalue.

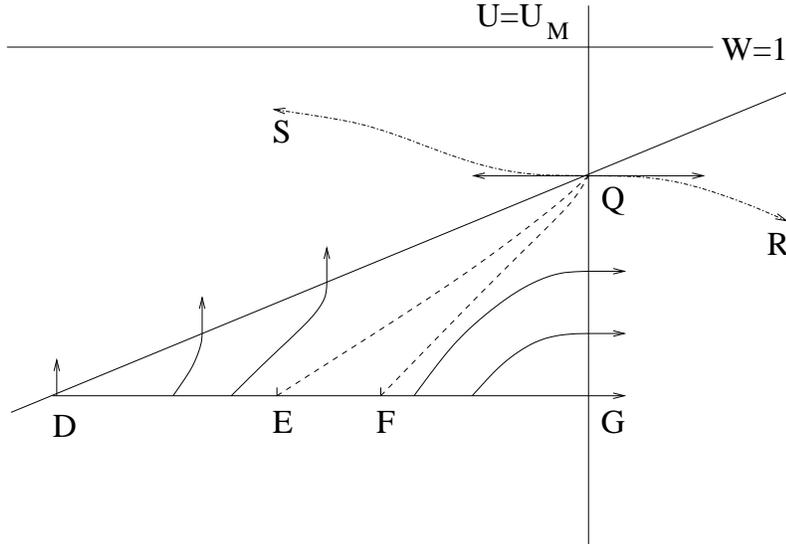
In this case we can use the Bendixon classification theorem, see Theorem 17.2, chapter X of [4], which says that *The local phase-portrait of an isolated critical point with a single non-zero characteristic root is one of the following three types: node, saddle-point (four separatrices), two hyperbolic sector and a fan (three separatrices)*.

In our case we are interested in proving that the critical point is not a node (in which case it would be an unstable node because of the positive eigenvalue a), and that one and only one of the separatrices belongs to the region \mathcal{T} .

We consider the case $Q = (U_+, W_+)$ with $U_+ = U_M$ and $W_+ < 1$. The other two cases being similar, we limit ourselves to indicate the possible differences in the proof.

Consider the segment line belonging to the line $W = W_+ - \varepsilon$, for some sufficiently small ε , and bounded by the line $U - LW =$

Figure 4: Local phase-portrait



$U_- - LW_-$ and $U = U_M$. Let us denote by D and G its extremal points. We now concentrate on the phase-portrait in the triangle DQG , see figure (4).

Trajectories enter the triangle from the DG side and leave it either from the DQ side or the GQ side. This implies that there exists at least a separatrix whose ω -set is the point Q ¹.

Together with the positivity of the non-zero eigenvalue, this excludes that Q is a node.

Then it remains the alternative between the saddle point and the

¹For sake of completeness let us give a proof of this claim.

Consider the points on the side DG ; the trajectory passing through D has “vertical” slope and the one from G has “horizontal” slope. So define $E = \sup\{P \in DG \mid \gamma^+(P) \cap DQ \neq \emptyset\}$ and $F = \inf\{P \in DG \mid \gamma^+(P) \cap GQ \neq \emptyset\}$ where $\gamma^+(P)$ denotes the trajectory traversed after P . Now suppose that $\gamma^+(E) \cap DQ = H \neq Q$. Take any point $K \in HQ$ and let $\gamma^-(E)$ be the trajectory traversed before K . $\gamma^-(K)$ cannot intersect GQ because here the backward dynamics is entering the triangle and it cannot intersect $\gamma^+(E)$. So it must intersect the side DG at a point *on the right* of E , thus contradicting the definition of E . The same holds for $\gamma^+(F)$.

case with two hyperbolic sectors and a fan. It turns out that both the cases can happen, depending on how we define the reaction terms $A(U)$ and $B(W)$ for $U > U_M$ and $W > 1$ respectively.

But what matters for our original problem is to exclude the possibility that the fan is contained in the triangle DQG . If this were the case the region between $\gamma^+(E)$ and $\gamma^+(F)$ would be an attractive fan, and all the trajectories outside this fan must be divided into two hyperbolic regions. But this is not the case because from the existence of the positive eigenvalue a we deduce the existence of two other separatrices tangent to the line $W = W_+$. This implies that, if a fan exists, it must be the region above the latter two separatrices and $\gamma^+(E)$ and $\gamma^+(F)$ coincide (i.e. $E = F$). The same is true if the equilibrium is a saddle point.

For the two cases with $W_+ = 1$ the analysis can be done in quite the same way, simplified by the fact that now the two half lines $W = 1$ originating from Q are trajectories.

3.3. Phase-portrait behaviour for different a

We consider now the behaviour of the solution of the initial value problem (11)-(12) with initial data $U(0) = 0$ and $W(0) = W_- < 1$, for different values of a .

We consider these solutions as long as their trajectories belong to the trapezoidal region \mathcal{T} and we set $\gamma^{\mathcal{T}} = \gamma^+(0, W_-) \cap \mathcal{T}$. Finally we notice that, in \mathcal{T} , $U' > 0$, so we can express the solution as $W = w_a(U)$ (we use the index a to stress the dependence on a .)

LEMMA 3.2. [Monotonicity] *If $a_1 < a_2$, and if $w_{a_1}(U_0) > w_{a_2}(U_0)$ for $U_0 \in [0, U_M)$, then*

$$w_{a_1}(U) > w_{a_2}(U), \quad (19)$$

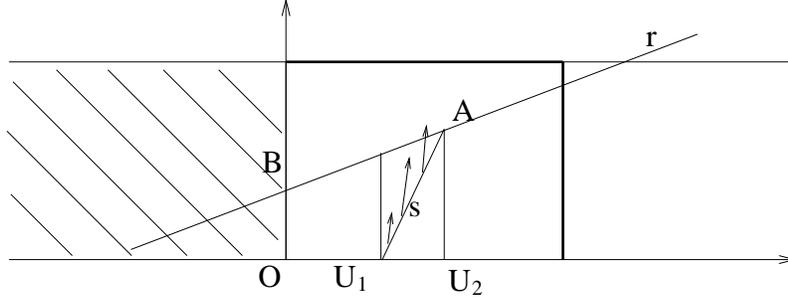
for any $U > U_0$ for which both solutions have trajectory in \mathcal{T} .

The proof follows considering that if the trajectories hit (or are tangent) for some value of U , say \bar{U} , then in that point we have

$$\frac{dw_{a_1}}{dU} = \frac{a_2^2}{a_1^2} \frac{dw_{a_2}}{dU} > \frac{dw_{a_2}}{dU}, \quad (20)$$

contradicting the hypothesis.

Figure 5: Phase-portrait for small a



LEMMA 3.3. **[Small a]** *If a is sufficiently small then, for any value of W_- , $\gamma^+(0, W_-)$ intersects the line r .*

Proof. With reference to figure (5), fix two values U_1 and U_2 in $(0, U_M)$ such that the lines $U = U_1$ and $U = U_2$ intersect the line r for values of W less than $1 - \varepsilon$ for some small positive ε . Then consider the region bounded by $U = U_1$, $U = U_2$, $W = 0$ and the line r .

In this region we have

$$0 \leq U - U_- - (LW - LW_-) \leq d \tag{21}$$

$$A(U)B(W) \geq \delta > 0 \tag{22}$$

for appropriate d and δ .

Let s be the segment line joining $(U_1, 0)$ and $A = (U_2, W_- + \frac{U_2 - U_-}{L})$.

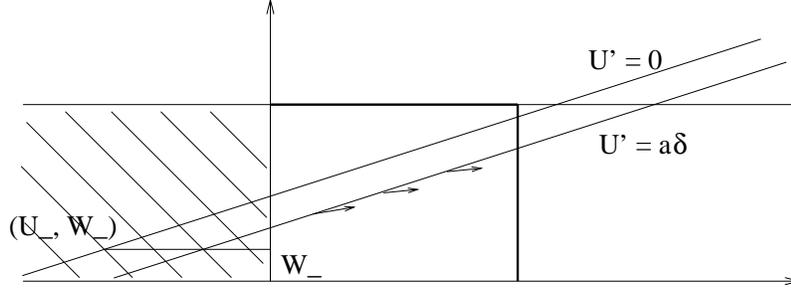
On s we have

$$\frac{dw_a}{dU} \geq \frac{1}{a^2} \frac{\delta}{d}. \tag{23}$$

Then, if a is small enough, $\frac{dw_a}{dU}$ is greater than the slope of s . It follows that the solutions can leave the region OU_1AB only crossing the line r . \square

LEMMA 3.4. **[Large a]** *For any (U_-, W_-) , with $U_- \leq 0$, there exists a sufficiently large a such that $\gamma^+(0, W_-)$ intersects the segment line $\{U = U_M, 0 < W < 1\}$.*

Figure 6: Phase-portrait for large a



Proof. Let $0 < \delta < -U_-$ and consider the points on the segment on the line r_δ of equation $U - LW = U_- - LW_- + \delta$ laying inside \mathcal{T} . Here we have

$$\frac{dw_a}{dU} < \frac{1}{a} \frac{\bar{A}\bar{B}}{a\delta} \tag{24}$$

where \bar{A} and \bar{B} are the maximal values of the functions A and B respectively. It follows immediately that we can choose a large enough to have $\frac{1}{a} \frac{\bar{A}\bar{B}}{a\delta} < \frac{1}{L}$, so that solutions entering \mathcal{T} at $U = 0$ below the line r_δ can leave \mathcal{T} only through the boundary $U = U_M$. \square

4. Existence and uniqueness of the wave

In the previous section we proved that, for any sufficiently large value of the speed a , there exists only one bounded solution of our initial value problem. Here we conclude the proof of Theorem (2.1), proving that there exists one and only one value of a such that the corresponding bounded solution originates from our initial condition.

Let us indicate by $\tilde{w}_a(U)$ the solution, corresponding to the speed a , such that $\lim_{U \rightarrow U_+} \tilde{w}_a(U) = W_+$ (i.e. the separatrix in \mathcal{T}) and by U_a the minimal value of U for which $(U, \tilde{w}_a(U))$ enters the region \mathcal{T} (if $U_a = 0$, then $\tilde{w}_a(U)$ corresponds to a travelling wave solution).

PROPOSITION 4.1. [Monotonicity of the separatrices] *If $a_1 < a_2$ then*

$$\tilde{w}_{a_1}(U) < \tilde{w}_{a_2}(U), \tag{25}$$

for any $U, \max\{U_{a_1}, U_{a_2}\} < U < U_M$.

Proof. Suppose that (25) is non true, then there exists U_0 such that $\tilde{w}_{a_1}(U_0) > \tilde{w}_{a_2}(U_0)$ (we can use the strict monotonicity: in fact, if we have $\tilde{w}_{a_1}(U) = \tilde{w}_{a_2}(U)$ for some U , then the solutions are strictly ordered in a right neighbourhood because of the derivative values.)

Then, according to Lemma 3.2, we have $\tilde{w}_{a_1}(U) > \tilde{w}_{a_2}(U)$ for $U_0 < U < U_M$.

Now let $W_0 \in (\tilde{w}_{a_2}(U_0), \tilde{w}_{a_1}(U_0))$ and let $w_{a_2}(U)$ be the solution corresponding to speed a_2 and initial condition $w_{a_2}(U_0) = W_0$. Then, Lemma 3.2 implies that

$$w_{a_2}(U) < \tilde{w}_{a_1}(U) \quad (26)$$

for $U > U_0$. But $W = w_{a_2}(U)$ stays above the separatrix $W = \tilde{w}_{a_2}(U)$ so it have to cross the line r for some $U < U_M$ contraddicting (26). \square

We now define a function $a \rightarrow P(a)$ which associates to each speed a the point $P(a) = (U_a, W_a)$ at which the separatrix $W = \tilde{w}_a(U)$ enters the region \mathcal{T} . Then for any positive a there exists $P(a) \in \{(U, W) \mid 0 \leq U < U_M, W = 0\} \cup \{(U, W) \mid U = 0, 0 \leq W < W_- - \frac{U_-}{L}\}$

PROPOSITION 4.2. [Continuity] $a \rightarrow P(a)$ is a continuous function.

Proof. For sake of simplicity we give the proof in the case $U_+ = U_M$ and $W_+ < 1$ and we take a large enough to have $\tilde{w}_a(0) = W_- > 0$. The proof in the other cases (for instance if $U_+ < U_M$ and $W_+ = 1$) needs only minor changes.

From Proposition 4.1 it turns out that P is a monotone increasing function, if we order the “entering” boundary of \mathcal{T} in clockwise sense starting from $(U_M, 0)$. Then, for any \bar{a} we have

$$P(\bar{a}^-) = \lim_{a \rightarrow \bar{a}^-} P(a) \leq P(\bar{a}) \leq \lim_{a \rightarrow \bar{a}^+} P(a) = P(\bar{a}^+) \quad (27)$$

Suppose now that one of the above inequalities is strict. We can assume without loss of generality that

$$P(\bar{a}^-) < P(\bar{a}). \quad (28)$$

Let $\{a_n\}$ be a sequence converging from below to \bar{a} . Then the corresponding sequence of functions $\{\tilde{w}_{a_n}\}$ is a monotone equibounded sequence and then is defined

$$w^-(U) = \lim_{a_n \rightarrow \bar{a}^-} \tilde{w}_{a_n}(U). \quad (29)$$

Now take a sequence $\{U_k\}$ converging from below to U_M . For any $U_k < U_M$, the functions \tilde{w}_{a_n} are equicontinuous in $[0, U_k]$, as well as their derivatives with respect to U (that because for $U \leq U_k$ the functions \tilde{w}_{a_n} are uniformly bounded away from $W = W_- + (U - U_-)/L$ so that the function $\frac{1}{a^2}(A(U)B(W))/[(U-LW)-(U_- - LW_-)]$ is uniformly Lipschitz continuous).

It follows that w^- is a solution of the differential equation (with $a = \bar{a}$) in $0 < U < U_k$ for any $U < U_k$ and then for any $U < U_M$.

Since $\lim_{U \rightarrow U_M} w^-(U) = W_+$, the curve $W = w^-(U)$ is the separatrix corresponding to $a = \bar{a}$, and must coincide with $\tilde{w}_{\bar{a}}$ contradicting the assumption (28). \square

These two propositions conclude the proof of theorem (2.1).

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