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## **Resolution of the Cauchy problem for several hyperbolic systems arising in chemical engineering**

by

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**ABSTRACT.** — This paper presents the thorough mathematical study of a classical model in chemical engineering: the Langmuir isotherm. This model has been studied by E. Canon for the distillation, and F. James for the chromatography. It is a system of  $n$  non linear conservation laws ( $n \geq 1$ ), which is shown to be strictly hyperbolic. The main property of this system is that its rarefaction and shock curves coincide, and moreover are straight lines. This implies a global existence result for the Riemann problem, as well as the convergence of the Godunov scheme. One can finally obtain the existence of an entropic weak solution for the Cauchy problem with any bounded variation initial data.

*Key words* : Hyperbolic systems, Riemann problem, Cauchy problem, strong Riemann invariants, Temple class, chemical engineering, Langmuir isotherm.

**RÉSUMÉ.** — Cet article présente l'étude mathématique complète d'un modèle d'équilibre diphasique classique en génie chimique : l'isotherme de Langmuir. Ce modèle, étudié par E. Canon pour la distillation et F. James

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pour la chromatographie, est fondé sur l'écriture d'un système de  $n$  équations de conservation non linéaires ( $n \geq 1$ ), dont on démontre la stricte hyperbolicité. La propriété fondamentale du système considéré est que ses courbes de détente et de choc coïncident, et sont des droites. On en déduit un résultat d'existence globale du problème de Riemann, ainsi que la convergence du schéma de Godunov. On obtient finalement l'existence d'une solution faible entropique au problème de Cauchy avec donnée initiale à variation bornée.

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## 1. INTRODUCTION

Two chemical engineering processes, distillation and chromatography, involve matter exchange to separate or analyse mixtures. Under some assumptions, *see* [V], [J], [C], one can model these processes by a system of first order non linear partial differential equations. We give here these systems, which are very close to each other. One can also mention the system of electrophoresis, which we shall not study in this paper but still have the same properties and for which our results remain true. Throughout this paper, we shall consider a mixture of  $M + 1$  chemical species, denoted with underscripts from 0 to  $M$ . These species will be called either "component" or "species".

In chromatography one of the species plays a particular part. One of the phases, which will be denoted 1 is a mobile fluid phase, carried along by a vector fluid. This vector fluid cannot change phase. It will be our species 0. Its concentration in phase 1 is assumed to be constant and is denoted by  $c_0^1$ . The second phase is stationary, fluid or solid. The fluid vector velocity is denoted by  $u$  and is assumed to be a positive constant. The time and space dependent function  $c_i^j$  is the concentration of component  $i$  in phase  $j$ . The material balance equations lead to

$$\frac{\partial c_i^1}{\partial z} + \frac{1}{u} \frac{\partial}{\partial t} \left( c_i^1 + \frac{1-\varepsilon}{\varepsilon} c_i^2 \right) = 0, \quad (1.1)$$

for  $i$  varying from 1 to  $M$ . In these equations,  $\varepsilon$  is the fractional void space of the chromatographic column. It is a constant strictly included between 0 and 1. We have here  $M$  equations and  $M + 1$  species. The last equation is simply given by

$$c_0^1 = \text{const.} \quad (1.2)$$

In a distillation column, the  $M + 1$  species can change phase. Moreover, both phases are mobile, and moving counter-current to each other. We have typically a vapor phase denoted 1, and a liquid phase, denoted 2. The variables are here the molar fractions  $x_i^j$  (component  $i$  in phase  $j$ ) defined by

$$x_i^j = \frac{c_i^j}{\sum_{m=0}^M c_m^j}$$

for  $i=0, \dots, M$  and  $j=1, 2$ . We have the following conservation laws, for  $i$  varying from 0 to  $M$ :

$$\frac{\partial}{\partial z} (-F_1 x_i^1 + F_2 x_i^2) + \frac{\partial}{\partial t} (f_1 x_i^1 + f_2 x_i^2) = 0, \quad (1.1')$$

where  $F_j$  is the molar flow in phase  $j$ , and  $f_j$  the hold-up rate in phase  $j$ , defined by

$$f_j = \frac{F_j}{u_j},$$

where  $u_j$  is the velocity in phase  $j$ . These quantities are positive constants. The definition of molar fractions involves

$$\sum_{m=0}^M x_m^j = 1, \quad (1.2')$$

so that the  $M + 1$  equations in (1.1') are not independent. From now we shall consider the system (1.1') restricted to the  $M$  equations  $1 \leq i \leq M$ . The bounds between (1.1) and (1.1') are obvious: by setting  $F_2 = 0$  in (1.1'), which only means that the phase 2 is stationary, we obtain again the system (1.1). The boundary conditions are still strongly different and rather more difficult in the case of distillation, *see* [C].

Now, we close our systems (1.1) and (1.1') by relating  $c_i^2$  (resp.  $x_i^2$ ) to the concentrations in mobile phase  $c_i^1$ ,  $i=1, \dots, M$  (resp. to the molar fractions in vapor phase  $x_i^1$ ,  $i=1, \dots, M$ ) with a function  $h_i$ , called isotherm of component  $i$ . From a general point of view, isotherms are obtained by thermodynamical considerations. Assuming both phases to be at thermodynamical equilibrium, we get relations analogous to the Gibbs relations (chemical potential equalities). These relations imply the existence of the isotherms, and some properties on their derivatives (*see* Kvaalen *et al.* [KNT], James [J]).

In this paper our purpose is to study one of these models of isotherm, very classical in chemical engineering: the Langmuir isotherm (1916). We go back to a study, originally due to Rhee, Aris and Amundson: *see*

[RAA1] for chromatography, or [RAA2] for counter-current chromatography. We propose a more formal proof of their results: hyperbolicity of the system, resolution in the large of the Riemann problem. Finally, using some results of Serre [Se], we get a global existence result for the Cauchy problem associated to systems (1.1) and (1.1').

## 2. ISOTHERM AND EQUILIBRIUM MATRIX

In terms of concentrations the Langmuir isotherm is given by:

$$c_i^2 = N \frac{K_i c_i^1}{1 + \sum_{m=1}^M K_m c_m^1}, \quad (2.1)$$

where  $N$  is a positive normalization constant such that  $c_i^2 = N x_i^2$ . In this formulation, the coefficients  $K_i$  are constants, which we shall call Langmuir coefficients, and satisfy:

$$0 < K_1 < \dots < K_M. \quad (2.2)$$

In terms of molar fractions the same isotherm becomes

$$x_i^2 = \frac{\beta_i x_i^1}{1 + \sum_{m=1}^M (\beta_m - 1) x_m^1}, \quad (2.1')$$

where the coefficients  $\beta_i$  are non-dimensional constants, and are the inverse of the relative volatilities. The bound between (2.1) and (2.1') is obvious. For example one can easily deduce (2.1') from (2.1) by using the definition of the molar fraction, and setting  $\beta_i = c_0^1 K_i$ . To simplify the calculus and homogenize our notations, we now introduce non-dimensional variables which we denote  $w_i$  for both systems:

$$w_i = K_i c_i^1 \quad (2.3)$$

$$w_i = (\beta_i - 1) x_i^1 \quad (2.3')$$

With these notations, systems (1.1) and (1.1') may be respectively rewritten as

$$\frac{\partial w_i}{\partial z} + \frac{1}{u} \frac{\partial}{\partial t} \left( w_i + \rho \frac{K_i w_i}{D(\mathbf{w})} \right) = 0, \quad (2.4)$$

where  $\rho = N \frac{1-\varepsilon}{\varepsilon}$ , and

$$\frac{\partial}{\partial z} \left( -F_1 w_i + F_2 \frac{\beta_i w_i}{D(\mathbf{w})} \right) + \frac{\partial}{\partial t} \left( f_1 w_i + f_2 \frac{\beta_i w_i}{D(\mathbf{w})} \right) = 0. \quad (2.4')$$

The function  $D(\mathbf{w})$  is given by

$$D(\mathbf{w}) = 1 + \sum_{i=1}^M w_i. \quad (2.5)$$

With the convention  $\beta_i = K_i$ , we introduce now the functions  $h_i$ ,  $i=1, \dots, M$ , deduced from the isotherms, and defined by

$$h_i(\mathbf{w}) = \frac{K_i w_i}{D(\mathbf{w})}. \quad (2.6)$$

Let  $\mathbf{h}$  be the vector valued function with components  $h_i$ ,  $i=1, \dots, M$ . We set

$$\begin{cases} \mathbf{f}(\mathbf{w}) = \mathbf{w} + \rho \mathbf{h}(\mathbf{w}), \\ \mathbf{f}_z(\mathbf{w}) = -F_1 \mathbf{w} + F_2 \mathbf{h}(\mathbf{w}), \\ \mathbf{f}_t(\mathbf{w}) = f_1 \mathbf{w} + f_2 \mathbf{h}(\mathbf{w}), \end{cases}$$

so that systems (2.4) et (2.4') can be rewritten as

$$\begin{aligned} \frac{\partial \mathbf{w}}{\partial z} + \frac{\partial}{\partial t} \mathbf{f}(\mathbf{w}) &= 0 \\ \frac{\partial}{\partial z} \mathbf{f}_z(\mathbf{w}) + \frac{\partial}{\partial t} \mathbf{f}_t(\mathbf{w}) &= 0 \end{aligned}$$

DEFINITION 2.1. — *The matrix  $J(\mathbf{w})$ , defined by:*

$$J(\mathbf{w}) = D(\mathbf{w}) \mathbf{h}'(\mathbf{w}), \quad (2.7)$$

*is called equilibrium matrix.*

LEMMA 2.1. — *If the equilibrium matrix is diagonalizable, then systems (2.4) and (2.4') are hyperbolic.*

*Proof. — Chromatography.*

The Jacobian matrix of system (2.4) is given by

$$L(\mathbf{w}) = I_M + \frac{\rho}{D(\mathbf{w})} J(\mathbf{w}), \quad (2.8)$$

where  $I_M$  is the identity matrix of  $\mathbb{R}^M$ . The result is obvious, and we have, if  $\lambda(\mathbf{w})$  is an eigenvalue of  $L(\mathbf{w})$ .

$$\lambda(\mathbf{w}) = 1 + \frac{\rho}{D(\mathbf{w})} \mu(\mathbf{w}), \quad (2.9)$$

where  $\mu(\mathbf{w})$  is an eigenvalue of  $J(\mathbf{w})$ .

*Distillation.*

For every regular solution, (2.4') can be rewritten as

$$\frac{\partial \mathbf{w}}{\partial t} + L(\mathbf{w}) \frac{\partial \mathbf{w}}{\partial z} = 0,$$

where the matrix  $L(\mathbf{w})$  is defined by

$$L(\mathbf{w}) = \left( f_2 \frac{J(\mathbf{w})}{D(\mathbf{w})} + f_1 I_M \right)^{-1} \left( F_2 \frac{J(\mathbf{w})}{D(\mathbf{w})} - F_1 I_M \right). \quad (2.8')$$

The system (2.4') is hyperbolic if  $L(\mathbf{w})$  is diagonalizable, so if  $J(\mathbf{w})$  is diagonalizable. We have the formula, analogous to (2.9):

$$\lambda(\mathbf{w}) = \frac{(-F_1 D(\mathbf{w}) + F_2 \mu(\mathbf{w}))}{(f_1 D(\mathbf{w}) + f_2 \mu(\mathbf{w}))}. \quad (2.9')$$

If  $\mu(\mathbf{w})$  is an eigenvalue of  $J(\mathbf{w})$ , with corresponding eigenvector  $r(\mathbf{w})$ , then  $r(\mathbf{w})$  is an eigenvector of  $L(\mathbf{w})$ , with corresponding eigenvalue  $\lambda(\mathbf{w})$ , defined by (2.9) for chromatography and by (2.9') for distillation.  $\blacklozenge$

Now, we just have to study the equilibrium matrix  $J(\mathbf{w})$  given by:

$$J(\mathbf{w}) = \begin{pmatrix} K_1 & 0 \\ & \ddots \\ 0 & K_M \end{pmatrix} - \frac{1}{D(\mathbf{w})} \begin{pmatrix} K_1 w_1 & \dots & K_1 w_1 \\ \vdots & & \vdots \\ K_M w_M & \dots & K_M w_M \end{pmatrix}. \quad (2.10)$$

It is clear that, if they exist, eigenvectors and eigenvalues of  $J(\mathbf{w})$  have to satisfy:

$$r_i(\mathbf{w})(K_i - \mu(\mathbf{w})) = \frac{1}{D(\mathbf{w})} K_i w_i s(\mathbf{r}(\mathbf{w})) \quad (2.11)$$

for  $i=1, \dots, M$ , where, if  $\mathbf{v}$  is a vector of  $\mathbb{R}^M$ ,

$$s(\mathbf{v}) = \sum_{i=1}^M v_i.$$

The Langmuir coefficients  $K_i$  will play a particular part in this study. Let us define  $\mathbb{E}_M = \{ \mathbf{w} \in \mathbb{R}^M; w_i > 0 \text{ for every } i \}$ .

PROPOSITION 2.1. — *For every  $\mathbf{w}$  in  $\mathbb{E}_M$ , the matrix  $J(\mathbf{w})$  has  $M$  strictly positive eigenvalues  $\mu_1(\mathbf{w}), \dots, \mu_M(\mathbf{w})$ , such that*

$$0 < \mu_1(\mathbf{w}) < K_1 < \mu_2(\mathbf{w}) < \dots < \mu_M(\mathbf{w}) < K_M \quad (2.12)$$

Before proving this proposition we give two liminar results.

LEMMA 2.2. — *Let  $\mathbf{r}(\mathbf{w})$  be an eigenvector of  $L(\mathbf{w})$ . Then  $s(\mathbf{r}(\mathbf{w})) \neq 0$ .*

*Proof.* — Let us assume that  $s(\mathbf{r}(\mathbf{w})) = 0$ . Then from (2.11), we have for all  $i$

$$r_i(\mathbf{w})(K_i - \mu(\mathbf{w})) = 0. \quad (2.13)$$

Since  $\mathbf{r}(\mathbf{w})$  is an eigenvector, there exists  $i$  such that  $r_i(\mathbf{w}) \neq 0$ . But since  $s(\mathbf{r}(\mathbf{w})) = 0$ , there exists another  $j \neq i$  such that  $r_j(\mathbf{w}) \neq 0$ . Then equality

(2.13) implies

$$\mu(\mathbf{w}) = K_i = K_j,$$

which cannot be true because the coefficients  $K_i$  are distinct.  $\blacklozenge$

LEMMA 2.3. —  $K_i$  is an eigenvalue for  $J(\mathbf{w})$  if and only if  $w_i = 0$ .

*Proof.* — Let us assume, for simplicity, that  $w_1 = 0$ . The matrix  $J(\mathbf{w})$  is then

$$J(\mathbf{w}) = \begin{pmatrix} K_1 & 0 & & 0 \\ 0 & K_2 & & \\ & & \ddots & \\ 0 & & & K_M \end{pmatrix} - \frac{1}{D(\mathbf{w})} \begin{pmatrix} 0 & \dots & 0 \\ K_2 w_2 & \dots & K_2 w_2 \\ \vdots & & \vdots \\ K_M w_M & \dots & K_M w_M \end{pmatrix}.$$

and it is obvious that  $K_1$  is eigenvalue.

On the other hand, if  $K_i$  is an eigenvalue, the left part of equality (2.11) is zero, so that  $w_i = 0$ .  $\blacklozenge$

*Proof of Proposition 2.1.* — From Lemma 2.3, in  $\mathbb{E}_M$ , no  $K_i$  is eigenvalue. Hence one may divide by  $K_i - \mu(\mathbf{w})$  in (2.11). Summing the  $M$  relations obtained, and simplifying by  $s(\mathbf{r}(\mathbf{w}))$ , which, from Lemma 2.2, is non zero, we get a characterization of the eigenvalues  $\mu(\mathbf{w})$  of  $J(\mathbf{w})$ :

$$\frac{1}{D(\mathbf{w})} \sum_{i=1}^M \frac{K_i w_i}{K_i - \mu(\mathbf{w})} = 1. \quad (2.14)$$

Let us now define the function  $\psi$  from  $\mathbb{R} \times \mathbb{R}^M$  to  $\mathbb{R}$  by:

$$\psi(\mu, \mathbf{w}) = \frac{1}{D(\mathbf{w})} \sum_{i=1}^M \frac{K_i w_i}{K_i - \mu} - 1. \quad (2.15)$$

To show Proposition 2.1 we just have to establish that the equation

$$\psi(\mu, \mathbf{w}) = 0$$

has  $M$  simple roots. Since we have

$$\psi'_\mu(\mu, \mathbf{w}) = \frac{1}{D} \sum_{i=1}^M \frac{K_i w_i}{(K_i - \mu)^2}, \quad (2.16)$$

which is strictly positive for  $\mathbf{w} \in \mathbb{E}_M$ , the function  $\mu \rightarrow \psi(\mu, \mathbf{w})$  is as in Figure 2.1, and the proof is complete.  $\blacklozenge$

*Remark.* — Because of Lemma 2.2 one can normalize the eigenvectors by

$$s(\mathbf{r}(\mathbf{w})) = 1.$$

Then, by comparing (2.11) and (2.14), we get a characterization of the eigenvectors of  $J(\mathbf{w})$ . If  $\mathbf{r}(\mathbf{w})$  is an eigenvector of  $J(\mathbf{w})$  with corresponding

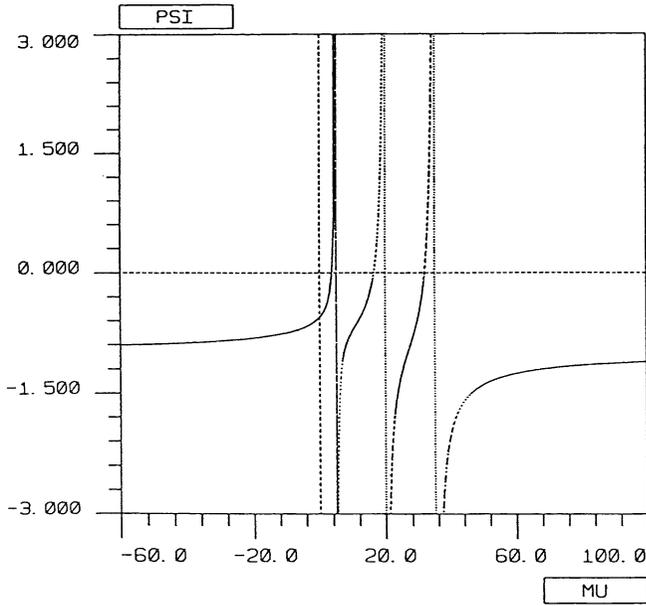


FIG. 2. 1. -  $K_1 = 5, K_2 = 20, K_3 = 35$ .

eigenvalue  $\mu(\mathbf{w})$ , we have indeed

$$r_i(\mathbf{w}) = \frac{1}{D(\mathbf{w})} \frac{K_i w_i}{K_i - \mu(\mathbf{w})}, \tag{2.17}$$

where  $\mu(\mathbf{w})$  is solution of (2.14).

We now give a result about the behavior of the characteristic fields of our systems.

PROPOSITION 2.2. - *For every point in  $\mathbb{E}_M$  the characteristic fields are genuinely nonlinear.*

*Proof.* - Let  $\mathbf{w} \in \mathbb{E}_M$ , and  $\mu$  be the associated solution of  $\psi(\mu, \mathbf{w}) = 0$ . From (2.16), we have that  $\psi'_\mu(\mu, \mathbf{w})$  is strictly positive, so that the implicit function theorem applies: we have the local existence of a function  $\mu(\mathbf{w})$ , with derivative given by

$$\mu'(\mathbf{w}) d\mathbf{w} = - \frac{1}{\psi'_\mu(\mu(\mathbf{w}), \mathbf{w})} \psi'_\mathbf{w}(\mu(\mathbf{w}), \mathbf{w}) d\mathbf{w}. \tag{2.18}$$

Besides, we have, for every  $v \in \mathbb{R}$ ,

$$\psi'_w(v, w) dw = \frac{1}{D(w)} \sum_{i=1}^M \frac{K_i dw_i}{K_i - v} - \frac{1}{D(w)^2} \left( \sum_{i=1}^M dw_i \right) \sum_{i=1}^M \frac{K_i w_i}{K_i - v},$$

which means, from (2.14)

$$\psi'_w(\mu(w), w) dw = \frac{1}{D(w)} \sum_{i=1}^M \frac{K_i dw_i}{K_i - \mu(w)} - \frac{1}{D(w)} \sum_{i=1}^M dw_i.$$

After simplifications we finally get

$$\psi'_w(\mu(w), w) dw = \frac{\mu(w)}{D(w)} \sum_{i=1}^M \frac{dw_i}{K_i - \mu(w)}. \tag{2.19}$$

Let  $r(w)$  be the eigenvector with associated eigenvalue  $\mu(w)$ . From relation (2.19) and using (2.11) one can immediately deduce

$$\psi'_w(\mu(w), w) r(w) = \frac{\mu(w)}{D(w)} \psi'_\mu(\mu(w), w) s(r(w)),$$

and thus

$$\mu'(w) r(w) = - \frac{\mu(w)}{D(w)} s(r(w)). \tag{2.20}$$

For the eigenvalues of Jacobian matrix  $L(w)$ , we finally obtain  
 – for chromatography, from (2.9)

$$\lambda'(w) r(w) = -2 \frac{\mu(w)}{D(w)^2} s(r(w)), \tag{2.21}$$

which is non zero, since  $\mu(w) > 0$  and  $s(r(w)) \neq 0$ ;

– for distillation, we use (2.9'), and we get (omitting for simplicity the dependences on  $w$ ),

$$\lambda' \cdot r = \frac{-F_1 D' \cdot r + F_2 \mu' \cdot r}{f_1 D + f_2 \mu} - \frac{-F_1 D + F_2 \mu}{(f_1 D + f_2 \mu)^2} (f_1 D' \cdot r + f_2 \mu' \cdot r),$$

From (2.20) and relation

$$D'(w) \cdot r(w) = s(r(w)),$$

we get after simplifications

$$\lambda'(w) \cdot r(w) = -2 \mu(w) \frac{f_1 F_2 + f_2 F_1}{(f_1 D(w) + f_2 \mu(w))^2} s(r(w)). \tag{2.21'}$$

All involved quantities being positive, the proof is complete. ♦

From (2.20), one can easily deduce the following result

**COROLLARY 2.1.** – Let  $\mu_k(w)$  be a simple eigenvalue of  $J(w)$ , and  $r_k(w)$  the corresponding eigenvector. Then the function  $g_k$ , defined by

$g_k(\mathbf{w}) = D(\mathbf{w})\mu_k(\mathbf{w})$ , is a  $k$ -Riemann invariant in the following sense:

$$g'_k(\mathbf{w}) \cdot \mathbf{r}_k(\mathbf{w}) = 0.$$

In other words,  $D(\mathbf{w})\mu_k(\mathbf{w})$  remains constant on the integral curve of the vector  $\mathbf{r}_k(\mathbf{w})$ .

We now come to study the rarefaction and shock curves. It will turn out that these curves coincide. We shall call them wave curves.

### 3. WAVE CURVES

The following proposition gives the main property of our systems.

PROPOSITION 3.1. — *The integral curves of the eigenvectors of  $L(\mathbf{w})$  are straight lines.*

*Proof.* — Once again we omit the dependence on  $\mathbf{w}$  in the calculations. On  $\mathbb{E}_M$ ,  $\mathbf{r}$  is characterized by

$$(K_i - \mu)r_i = \frac{1}{D}K_i w_i s(\mathbf{r}).$$

Taking the derivative in the direction  $\mathbf{r}$ , we get:

$$-\mu' \cdot \mathbf{r} r_i + (K_i - \mu)r'_i \cdot \mathbf{r} = \frac{1}{D}K_i w_i s(\mathbf{r}' \cdot \mathbf{r}) + \frac{1}{D}K_i r_i(\mathbf{r}) - \frac{1}{D^2}K_i w_i s(\mathbf{r})^2.$$

Replacing  $\mu' \cdot \mathbf{r}$  by its value (2.20), it becomes

$$(K_i - \mu)r'_i \cdot \mathbf{r} = \frac{1}{D}K_i w_i s(\mathbf{r}' \cdot \mathbf{r}) + \frac{1}{D}(K_i - \mu)r_i s(\mathbf{r}) - \frac{1}{D^2}K_i w_i s(\mathbf{r})^2.$$

In view of (2.11), we have then

$$(K_i - \mu)r'_i \cdot \mathbf{r} = \frac{1}{D}K_i w_i s(\mathbf{r}' \cdot \mathbf{r}).$$

In matrix form, this result becomes:

$$(J - \mu)\mathbf{r}' \cdot \mathbf{r} = 0,$$

in other words, the vector  $\mathbf{r}' \cdot \mathbf{r}$  is an eigenvector of  $J$  associated with the eigenvalue  $\mu$ , and thus colinear to  $\mathbf{r}$ . Finally on the whole integral curve of vector  $\mathbf{r}$ , we have

$$\frac{d}{d\tau}\mathbf{r}(\mathbf{w}(\tau)) = \alpha(\tau)\mathbf{r}(\mathbf{w}(\tau)).$$

This differential equation can be integrated:

$$\mathbf{r}(\mathbf{w}(\tau)) = c(\tau)\mathbf{r}(\mathbf{w}(0)),$$

where  $c(\tau) = \exp\left(\int_0^\tau \alpha(s) ds\right)$ . By definition of the integral curve of the vector  $r$ , we finally have

$$\frac{d\mathbf{w}(\tau)}{d\tau} = \mathbf{r}(\mathbf{w}(\tau)) = c(\tau) \mathbf{r}(\mathbf{w}(0)),$$

and the proof is complete.  $\blacklozenge$

**COROLLARY 3.1.** — *The rarefaction curves of systems (2.4) and (2.4') are straight lines.*

Systems with rarefaction curves as in Corollary 3.1 have been studied by Temple [T] and Serre [Se]. The notion of strict Riemann invariant (see [Sm]), which we now recall, arises naturally in this study.

**DEFINITION 3.1.** — *We call strict Riemann invariant a function  $v$  from  $\mathbb{R}^M$  to  $\mathbb{R}$ , whose gradient is a left eigenvector of  $L(w)$  [equivalently  $J(w)$ ]:*

$$v'(\mathbf{w}) \mathbf{J}(\mathbf{w}) = \mu(\mathbf{w}) v'(\mathbf{w}).$$

In the case of genuinely non linear characteristic fields, Temple has shown the equivalence of the three following assertions:

1. The integral curves of eigenvectors are straight lines.
2. On a rarefaction curve the system reduces to a single scalar conservation law.
3. Shock and rarefaction curves coincide.

Assertion 2 implies that the systems become uncoupled in finite time (see [Se]). According to Serre, we shall call an uncoupled system any system verifying 1, 2 or 3. For the systems of chromatography and distillation, we shall directly obtain assertions 2 and 3.

**PROPOSITION 3.2.** — *Let  $\mu(\mathbf{w})$  be a simple eigenvalue of  $\mathbf{J}(\mathbf{w})$ . Then it is a strict Riemann invariant for the corresponding characteristic field.*

*Proof.* — Using (2.18), we show that the  $i$ -th component of  $\mu'(\mathbf{w})$  is given by

$$\mu'_i(\mathbf{w}) = - \frac{1}{\psi'_\mu} \frac{1}{D(\mathbf{w})} \frac{1}{K_i - \mu(\mathbf{w})}. \quad (3.1)$$

Let us denote by  $J^i$  the  $i$ -th column vector of  $\mathbf{J}(\mathbf{w})$ : we have, for  $m = 1, \dots, M$

$$J_m^i = \delta_{im} K_i - \frac{1}{D(\mathbf{w})} K_m w_m,$$

where  $\delta_{im}$  is the Kronecker symbol. Again from (2.18), we obtain

$$\mu'(\mathbf{w}) J^i = - \frac{1}{\psi'_\mu} \frac{1}{D(\mathbf{w})} \left[ \frac{K_i}{K_i - \mu(\mathbf{w})} - \frac{1}{D(\mathbf{w})} \sum_{m=1}^M \frac{K_m w_m}{K_m - \mu(\mathbf{w})} \right].$$

But  $\mu(\mathbf{w})$  satisfies (2.14), so

$$\mu'(\mathbf{w})\mathbf{J}^i = - \frac{1}{\psi'_\mu} \frac{1}{D(\mathbf{w})} \frac{\mu(\mathbf{w})}{K_i - \mu(\mathbf{w})}. \tag{3.2}$$

By comparing (3.1) and (3.2), we have, component by component, Proposition 3.2.  $\blacklozenge$

We want now to study the shock curves. Let us recall first that, given two states  $\mathbf{w}^g$  et  $\mathbf{w}^d$  related by a discontinuous solution of the system (2.4), the velocity  $\sigma$  of the discontinuity has to satisfy the Rankine-Hugoniot jump condition

$$\sigma(\mathbf{w}^g - \mathbf{w}^d) = \mathbf{f}(\mathbf{w}^g) - \mathbf{f}(\mathbf{w}^d). \tag{3.3}$$

For the system of distillation, this condition becomes

$$\sigma(\mathbf{f}_z(\mathbf{w}^g) - \mathbf{f}_z(\mathbf{w}^d)) = \mathbf{f}_t(\mathbf{w}^g) - \mathbf{f}_t(\mathbf{w}^d). \tag{3.3'}$$

PROPOSITION 3.3. — *Assume that the two states  $\mathbf{w}^g$  and  $\mathbf{w}^d$  belong to a rarefaction curve of the system. Let  $\mu$  be the corresponding eigenvalue. The velocity  $\sigma$  is given by*

— chromatography

$$\sigma = 1 + \rho\tau; \tag{3.4}$$

— distillation

$$\sigma = \frac{-F_1 + F_2 \tau}{f_1 + f_2 \tau}, \tag{3.4'}$$

where  $\tau$  is given by

$$\tau = \frac{\mu(\mathbf{w}^g)}{D(\mathbf{w}^d)} = \frac{\mu(\mathbf{w}^d)}{D(\mathbf{w}^g)}. \tag{3.5}$$

*Proof.* — Using (3.4) and (3.4'), the Rankine-Hugoniot condition can be rewritten as

$$\tau(\mathbf{w}^g - \mathbf{w}^d) = \mathbf{h}(\mathbf{w}^g) - \mathbf{h}(\mathbf{w}^d).$$

Component by component, this relation gives

$$\begin{aligned} \tau(w_m^g - w_m^d) &= \frac{K_m w_m^g}{D(\mathbf{w}^g)} - \frac{K_m w_m^d}{D(\mathbf{w}^d)} \\ &= K_m \frac{w_m^g D(\mathbf{w}^d) - w_m^d D(\mathbf{w}^g)}{D(\mathbf{w}^g) D(\mathbf{w}^d)}. \end{aligned}$$

Inserting  $w_m^g D(\mathbf{w}^d) - w_m^d D(\mathbf{w}^g)$  in the numerator on the right handside of this equation, we get

$$\tau(w_m^g - w_m^d) = \frac{1}{D(\mathbf{w}^d)} \left[ K_m (w_m^g - w_m^d) - \frac{K_m w_m^g}{D(\mathbf{w}^g)} \sum_{k=1}^M (w_k^g - w_k^d) \right].$$

This relation is to compare with (2.11): it establishes that the vector  $(\mathbf{w}^g - \mathbf{w}^d)$  is an eigenvector of  $J(\mathbf{w}^g)$ , associated with the eigenvalue  $\tau D(\mathbf{w}^d)$ . Thus, we have  $\mu(\mathbf{w}^g) = \tau D(\mathbf{w}^d)$ . For every state  $\mathbf{w}^d$ , the vector  $(\mathbf{w}^g - \mathbf{w}^d)$  is colinear to  $\mathbf{r}(\mathbf{w}^g)$ . Thus, the shock curve through  $\mathbf{w}^g$  is a straight line in direction  $\mathbf{r}(\mathbf{w}^g)$ . Moreover it coincides with the rarefaction curve through  $\mathbf{w}^g$ . From Corollary 2.1,  $D\mu$  remains constant along this straight line. In particular  $D(\mathbf{w}^d)\mu(\mathbf{w}^d) = D(\mathbf{w}^g)\mu(\mathbf{w}^g)$ . We thus deduce (3.5):

$$\tau = \frac{\mu(\mathbf{w}^g)}{D(\mathbf{w}^d)} = \frac{\mu(\mathbf{w}^d)}{D(\mathbf{w}^g)}. \quad \blacklozenge$$

Proposition 3.3 shows that the integral curve of vector  $\mathbf{r}_i(\mathbf{w}^g)$ , which is a straight line, contains both the  $i$ -rarefaction curve and the  $i$ -shock curve. We shall call it the  $i$ -wave curve.

We now give a criterion selecting which part of the  $i$ -shock curve is admissible. Let us recall the classical conditions for a shock to be admissible (Lax[L]). If the system is strictly hyperbolic, a  $i$ -shock between  $\mathbf{w}^g$  and  $\mathbf{w}^d$ , moving with velocity  $\sigma_i$ , is said to be admissible if and only if

$$\begin{aligned} \lambda_i(\mathbf{w}^g) &> \sigma_i > \lambda_i(\mathbf{w}^d) \\ \lambda_{i-1}(\mathbf{w}^g) &< \sigma_i < \lambda_{i+1}(\mathbf{w}^d) \end{aligned}$$

PROPOSITION 3.4. — *In a point of strict hyperbolicity a  $i$ -shock is admissible if and only if  $\mu_i(\mathbf{w}^g) > \mu_i(\mathbf{w}^d)$ .*

*Proof.* — Relations (2.9) and (2.9') on the one hand, (3.4) and (3.4') on the other, can be rewritten as

$$\begin{aligned} \lambda(\mathbf{w}) &= \alpha \left( \frac{\mu(\mathbf{w})}{D(\mathbf{w})} \right) \\ \sigma &= \alpha \left( \frac{\mu(\mathbf{w}^g)}{D(\mathbf{w}^d)} \right) = \alpha \left( \frac{\mu(\mathbf{w}^d)}{D(\mathbf{w}^g)} \right). \end{aligned}$$

The function  $\alpha$  is defined by

$$\begin{aligned} \alpha(\zeta) &= 1 + \rho \zeta \quad \text{for chromatography,} \\ \alpha(\zeta) &= \frac{-F_1 + F_2 \zeta}{f_1 + f_2 \zeta} \quad \text{for distillation.} \end{aligned}$$

In both cases, the function  $\alpha$  is strictly increasing. The first Lax condition involves in particular

$$\alpha \left( \frac{\mu_i(\mathbf{w}^g)}{D(\mathbf{w}^g)} \right) > \alpha \left( \frac{\mu_i(\mathbf{w}^d)}{D(\mathbf{w}^g)} \right).$$

One can immediately deduce that  $\mu_i(\mathbf{w}^g) > \mu_i(\mathbf{w}^d)$ .

On the other hand, if  $\mu_i(\mathbf{w}^g) > \mu_i(\mathbf{w}^d)$ , we get trivially the first Lax condition. To obtain the second shock condition, we notice that  $\mu_{i-1}$  is a

$(i-1)$ -strict Riemann invariant (Proposition 3.2). In particular,  $\mu_{i-1}$  remains constant along the  $i$ -wave curve, so that

$$\mu_{i-1}(\mathbf{w}^g) = \mu_{i-1}(\mathbf{w}^d).$$

Thus, if  $\mathbf{w}^d$  is a point of strict hyperbolicity, we have

$$\mu_{i-1}(\mathbf{w}^g) = \mu_{i-1}(\mathbf{w}^d) < \mu_i(\mathbf{w}^d).$$

The function  $\alpha$  being strictly increasing, one can deduce

$$\alpha\left(\frac{\mu_{i-1}(\mathbf{w}^g)}{D(\mathbf{w}^g)}\right) < \alpha\left(\frac{\mu_i(\mathbf{w}^d)}{D(\mathbf{w}^g)}\right),$$

which means

$$\lambda_{i-1}(\mathbf{w}^g) < \sigma_i,$$

which is nothing but the second Lax condition. We proceed on the same way to get the right part of the Lax condition.  $\blacklozenge$

In short, the  $i$ -wave curve through a point  $\mathbf{w}^g$  in  $\mathbb{E}_M$  is a straight line; a point  $\mathbf{w}^d$  of this straight line is connected to  $\mathbf{w}^g$  by

a  $i$ -rarefaction if  $\mu_i(\mathbf{w}^g) < \mu_i(\mathbf{w}^d)$ ;

a  $i$ -shock if  $\mu_i(\mathbf{w}^g) > \mu_i(\mathbf{w}^d)$ .

With these results, we can now start to study the Riemann problem.

#### 4. THE RIEMANN PROBLEM

We want to show first that the equation (2.14) giving the eigenvalues of  $J(\mathbf{w})$  defines in fact a global change of variable mapping the quadrant  $\mathbb{E}_M$  onto a rectangle parallelogram of  $\mathbb{R}^M$ . Equation (2.14) is indeed equivalent to the algebraic equation  $P(\mu) = 0$ , where  $P$  is nothing but the characteristic polynomial of  $J(\mathbf{w})$ :

$$P(\mu) = \prod_{i=1}^M (K_i - \mu) - \frac{1}{D(\mathbf{w})} \sum_{i=1}^M K_i w_i \prod_{j \neq i} (K_j - \mu). \tag{4.1}$$

Notice here that (2.14) is only defined on the domain of strictly positive quantities  $\mathbb{E}_M$ , while, in view of Lemma 2.3, the algebraic equation  $P(\mu) = 0$  is also defined on the boundary of the domain. Let us call  $\mathcal{H}$  the function from  $\mathbb{E}_M$  into  $\mathbb{R}^M$ , which to  $\mathbf{w}$  associates the corresponding eigenvalues of  $J(\mathbf{w})$ .

PROPOSITION 4.1. — *The function  $\mathcal{H}$  is an homeomorphism from  $\mathbb{E}_M$  onto the set  $C_M$  defined by*

$$0 < y_1 < K_1 < \dots < y_M < K_M, \tag{4.2}$$

and the inverse homeomorphism is given by the following explicit formula:

$$w_i = K_i \frac{\prod_{j=1}^M (1 - (K_i/y_j))}{\prod_{j \neq i} (1 - (K_i/K_j))}. \tag{4.3}$$

*Proof.* – First, we prove (4.3). One can notice that the roots of  $P(\mu)=0$  are precisely the inverses of the roots of the equation  $Q(v)=0$ , where  $Q$  is the polynom defined by:

$$Q(v) = \prod_{i=1}^M (vK_i - 1) - \frac{v}{D} \sum_{i=1}^M K_i w_i \prod_{j \neq i} (vK_j - 1).$$

Let us call  $y_i$  the roots of  $P$ , we have

$$Q(v) = a_M \prod_{i=1}^M \left( v - \frac{1}{y_i} \right),$$

where  $a_M$  is the coefficient of the term  $v^M$  in  $Q$ , given by

$$\begin{aligned} a_M &= \prod_{i=1}^M K_i - \frac{1}{D} \sum_{i=1}^M K_i w_i \prod_{i \neq j} K_j \\ &= \frac{1}{D} \prod_{i=1}^M K_i. \end{aligned}$$

Comparing the two above relations, we get

$$a_M \prod_{i=1}^M \left( v - \frac{1}{y_i} \right) = \prod_{i=1}^M (vK_i - 1) - \frac{v}{D} \sum_{i=1}^M K_i w_i \prod_{j \neq i} (vK_j - 1).$$

Setting  $v = 1/K_i$ , the only term of the right handside which is non zero is the term with subscript  $i$ . We get then by replacing  $a_M$  by its value above

$$\prod_{i=1}^M K_i \cdot \prod_{i=1}^M \left( \frac{1}{K_i} - \frac{1}{y_i} \right) = w_i \prod_{j \neq i} \left( \frac{K_i}{K_j} - 1 \right).$$

From this equality, one can now easily deduce (4.3). On this formula it is obvious that  $\mathcal{H}$  is one to one, and that  $\mathcal{H}^{-1}$  is continuous. The proof is complete. ♦

We state here the formulas given in [RAA1] or [RAA2]. Figures 4.1 a and 4.1 b show respectively the wave curves in the space of conservative variables  $w_i$ , and their images by the transformation  $\mathcal{H}$  in the space of strict Riemann invariants.

Figure 4.2 shows the set  $C_3$ . Notice the non strict hyperbolicity points appearing on the boundary.

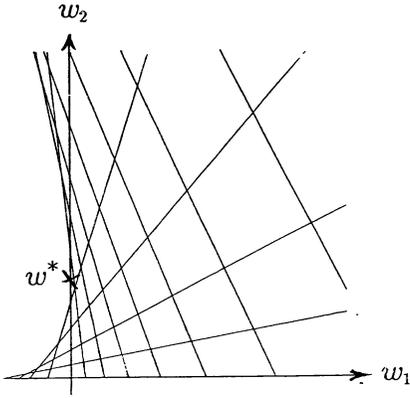


FIG. 4.1 a.

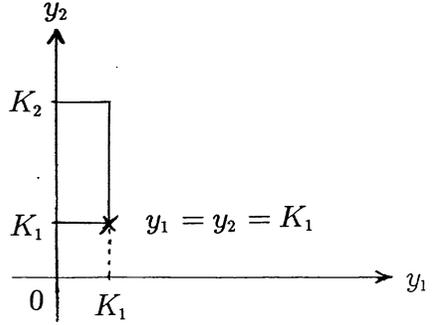


FIG. 4.1 b.

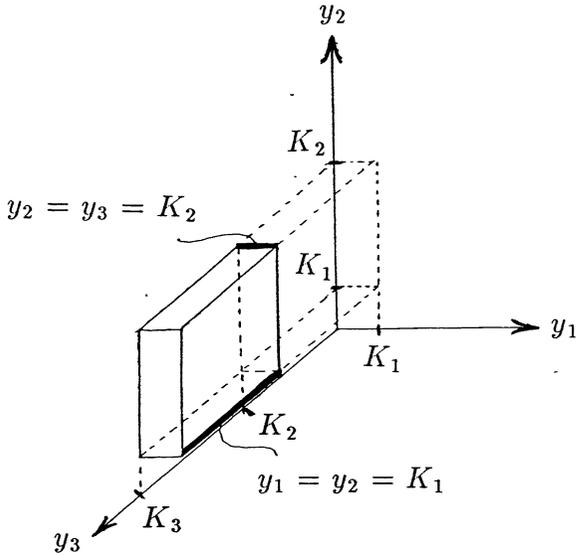


FIG. 4.2.

The transformation  $\mathcal{H}$  associates to each point  $\mathbf{w}$  of  $\mathbb{E}_M$  a point  $\mathbf{y}$  of  $\mathbb{C}_M$  such as

$$y_i = \mu_i(\mathbf{w}), \quad i = 1, \dots, M. \tag{4.4}$$

Let  $\mathbf{w}^g$  et  $\mathbf{w}^d$  be two states on the  $i$ -wave curve. To these points correspond  $\mathbf{y}^g$  and  $\mathbf{y}^d$ , satisfying (4.4). In view of Proposition 2.2, we have that for

every  $j \neq i$ ,  $\mu_j$  is invariant on the  $i$ -wave curve. Hence, both points  $\mathbf{y}^g$  and  $\mathbf{y}^d$  satisfy:

$$y_j^g = y_j^d, \quad j \neq i. \tag{4.5}$$

In other words, we have

LEMMA 4.1. — *The image of the  $i$ -wave curve by the homeomorphism  $\mathcal{H}$  is a straight line parallel to the  $i$ -th coordinate axis.*

More precisely, the image of the part of the  $i$ -wave contained in  $\mathbb{E}_M$  is the segment

$$K_{i-1} < y_i < K_i,$$

where  $K_0 = 0$ .

We are now able to give the main result of this paper, the global explicit resolution of the Riemann problem.

THEOREM 4.1 (Resolution of the Riemann problem in  $\mathbb{E}_M$ ). — *Let us consider two states  $\mathbf{w}^g$  and  $\mathbf{w}^d$  in  $\mathbb{E}_M$ . Then there exists an unique solution to the Riemann problem associated to  $\mathbf{w}^g$  and  $\mathbf{w}^d$ , consisting of at most  $M + 1$  constant states connected by a shock or a rarefaction wave.*

*Proof.* — The uniqueness of that kind of solution is a general result (see [Sm]). The existence comes from the fact that to  $\mathbf{w}^g$  and  $\mathbf{w}^d$  correspond two vectors  $\mathbf{y}^g$  and  $\mathbf{y}^d$ , belonging to the interior of the parallelogram  $C_M$ . Hence, there exists in  $C_M$  a path consisting of segments parallel to the coordinate axes and connecting  $\mathbf{y}^g$  to  $\mathbf{y}^d$ . We thus define  $M + 1$  points  $\mathbf{y}^i$ ,  $i = 0, \dots, M$ , with  $\mathbf{y}^0 = \mathbf{y}^g$ , and  $\mathbf{y}^M = \mathbf{y}^d$ . To each  $\mathbf{y}^i$  corresponds a state  $\mathbf{w}^i \in \mathbb{E}_M$ . We construct a self-similar solution to the Riemann problem by joining for every  $i$   $\mathbf{w}^{i-1}$  to  $\mathbf{w}^i$  by

- a  $i$ -rarefaction if  $y_i^{i-1} < y_i^i$ , i. e. if  $\mu_i(\mathbf{w}^{i-1}) < \mu_i(\mathbf{w}^i)$ ;
- a  $i$ -shock if  $y_i^{i-1} > y_i^i$ , i. e. if  $\mu_i(\mathbf{w}^{i-1}) > \mu_i(\mathbf{w}^i)$ .

From Proposition 3.4, the  $i$ -shock is admissible in the sense of Lax. ♦

Let us set  $\xi = t/z$ . Theorem 4.1 defines a self-similar solution to the Riemann problem, denoted  $\mathbf{W}(\xi)$ , without any restrictive condition on the initial data. This global existence result and the following stability theorem will lead us to a global existence result for the Cauchy problem.

THEOREM 4.2 ( $L^\infty$  and BV Stability). — *The resolution of the Riemann problem is stable in  $L^\infty$  and BV: we have for every  $i$*

$$\left. \begin{aligned} \text{Min}(\mu_i(\mathbf{w}^g), \mu_i(\mathbf{w}^d)) \leq \mu_i(\mathbf{W}(\xi)) \leq \text{Max}(\mu_i(\mathbf{w}^g), \mu_i(\mathbf{w}^d)) \\ \text{VT}(\mu_i(\mathbf{W}(\xi)) = |\mu_i(\mathbf{w}^g) - \mu_i(\mathbf{w}^d)| \end{aligned} \right\} \tag{4.6}$$

*Proof.* — The function  $\mu_i$  is constant excepted on the  $i$ -wave, where it is a monotone fonction of  $\xi$ , taking values in the segment  $[\mathbf{w}^i, \mathbf{w}^{i+1}]$ . Monotonicity obviously involves (4.6). ♦

*Remarks.* — 1. The  $L^\infty$  stability theorem leads to a result of invariance of the quadrant  $\mathbb{E}_M$ . If  $M$  species are present at the time  $t=0$ , we cannot “loose” one of these species by solving the Riemann problem. This property is transmitted to the Cauchy problem.

2. By working in variables  $w_i$ , we have lost of view the molar fractions. One can do all the above calculus in terms of molar fractions and get the same results. Still, the invariance of the quadrant  $\mathbb{E}_M$  becomes then the invariance of the molar fractions simplex defined by

$$S_M = \left\{ \mathbf{x} \in \mathbb{R}^{M+1}; x_m > 0 \text{ et } \sum_{m=0}^M x_m = 1 \right\}.$$

For the details of calculus, see [C].

Theorem 4.2 allows us to establish the  $L^\infty$  and BV stability of schemes based on the resolution of the Riemann problem: Godunov scheme, Glimm and Lax-Friedrichs schemes. To any couple  $(\Delta t, \Delta z)$ , where  $\Delta z$  is a space step and  $\Delta t$  a time step, these schemes associate a sequence of approximate solutions  $\tilde{\mathbf{w}}$  of systems (2.4) and (2.4'), provided that they satisfy the so-called Courant-Friedrichs-Lewy condition (CFL condition):

$$\frac{\Delta z}{\Delta t} < \text{Max}_{m=1, \dots, M} \left| \text{Sup}_{\mathbf{w}} \lambda_k(\mathbf{w}) \right|.$$

**THEOREM 4.3.** — *Let us assume the CFL condition to be satisfied. Then, we have the two following properties:*

1.  $L^\infty$  Stability: the Godunov scheme defines a sequence  $(\mathbf{w}_j^{n+1}; j \in \mathbb{Z}, n \in \mathbb{N})$  which takes values in  $\mathcal{H}^{-1}(\mathcal{H}(\mathbf{w}^0(t)))$ .
2. Decrease of the strict Riemann invariants: the functions

$$z \rightarrow \text{TV}(\mu_i(\tilde{\mathbf{w}}(\cdot, z))),$$

for  $i=1, \dots, M$ , are decreasing.

The proof of this result is rather technical, and we shall not give it there. One can refer to [Se] for the case of two by two systems. In any dimension the proof is strictly analogous to the one of Serre. For details, see [C] and [J].

This theorem involves BV estimations on the first order derivatives of the approximate solution  $\tilde{\mathbf{w}}$ . We define a sequence of functions  $\tilde{\mathbf{w}}_{\Delta z, \Delta t}$ , by associating to every couple  $(\Delta t, \Delta z)$  satisfying the CFL condition, the approximate solution computed by the Godunov scheme. We prove then that from this sequence one can extract a subsequence which converges in  $L^1_{loc}$ , in  $L^\infty$  weak star, and for almost every couple  $(t, z)$ . We obtain then the convergence of the Godunov scheme to an entropic solution  $\mathbf{w}$

of the systems, satisfying

$$\frac{\partial U(\mathbf{w})}{\partial z} + \frac{\partial F(\mathbf{w})}{\partial t} \leq 0$$

for any entropy  $U$  verifying:

- for chromatography,  $U$  is convex with respect to  $\mathbf{w}$ ;
- for distillation,  $U$  is convex with respect to  $\mathbf{f}_i(\mathbf{w})$ .

Finally, we have

**THEOREM 4.4.** – *Systems (2.4) and (2.4'), with a Cauchy condition  $\mathbf{w}(0, t) = \mathbf{w}^0(t)$ , where  $\mathbf{w}^0$  is of bounded variation, have a weak solution in  $]0, L[ \times \mathbb{E}_M$ , for every  $L > 0$ . Moreover this is an entropic solution.*

The results stated above for the Godunov scheme are also available for Glimm and Lax-Friedrichs schemes. The complete explicit resolution of the Riemann problem allows to construct an exact Riemann solver for the system of distillation. For chromatography, the situation is still simpler, since all eigenvalues are positive, so that the Godunov scheme reduces to a simple upwind scheme. Once again, we refer to [C] and [J] for details about schemes and calculus, and for numerical results.

## 5. CONCLUSION

Systems of conservation laws arising in chromatography and distillation allow a thorough mathematical study. The main property is the fact that rarefaction and shock curves coincide and are straight lines. We have then a behavior similar to the scalar case, and can apply similar techniques. Our systems are the only systems of more than two equations for which an existence result for the Cauchy problem and the convergence of the Godunov scheme have been obtained, without any assumption on the initial data. The explicit resolution of the Riemann problem also appears to be an excellent tool to valid numerical schemes. We finish by noticing that these systems may seem like purely academic examples. Still, they have a precise physical meaning, and the Langmuir isotherm is widely used in chemical engineering.

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