THE ROLE OF NON-EQUILIBRIUM THERMODYNAMICS IN COMPOSITIONAL MODELING

WANDERSON LAMBERT, DAN MARCHESIN AND JOHANNES BRUINING

ABSTRACT. We show how to derive compositional models from balance models including source terms representing mass transfer between phases. Mass transfer rate is taken proportional to the deviation from thermodynamic equilibrium. In the balance models, the mass transfer is very fast and local thermodynamic equilibrium is quickly attained. The derivation is done by means of an asymptotic expansion where the small parameter is the time scale of mass transfer relative to the hydrodynamical time scale. The new theory is illustrated by an example of thermal flow of steam, nitrogen and water in a porous medium, which can be useful in for soil remediation.

1. INTRODUCTION

Multiphase fluid flows with mass transfer between different phases are governed by compositional models, in the context of petroleum engineering. These are evolution equations that represent the conservation of mass of each chemical component, supplemented by equations of state and thermodynamic relationships. Of course, such models support rarefactions and shocks.

A more fundamental formulation of such flows is given by balance equations for each component in each phase, with stiff source terms representing mass transfer of components between phases. The form of these transfer terms is dictated by the thermodynamics: they vanish precisely under local thermodynamic equilibrium. The balance systems can be written in the following form, for $j = 1, \cdots, l$ and $i = l+1, \cdots, m+1$:

$$\frac{\partial}{\partial t}\mathcal{G}_j(\mathcal{V}) + \frac{\partial}{\partial x}u\mathcal{F}_j(\mathcal{V}) = \hat{q}_j(\mathcal{V})/\epsilon, \tag{1.1}$$

$$\frac{\partial}{\partial t}\mathcal{G}_i(\mathcal{V}) + \frac{\partial}{\partial x}u\mathcal{F}_i(\mathcal{V}) = 0. \tag{1.2}$$

This is a multi-scale problem, because ϵ is very small; this quantity is the time scale of physical phase changes that are active in non-equilibrium regions. We include ϵ to guarantee that $\hat{q}_j$ do not exceed the order of unity. The source terms $\hat{q}_j(\mathcal{V})/\epsilon$ represent mass transfer rates of chemical species between different phases. In these systems the total volume is not conserved, so the Darcy speed u representing total volumetric flow rate, which appears in a particular way within the flux terms, is not constant, generically, contrary to the case of the classical fractional flow theory in porous media. In (1.1)-(1.2), generically, we have saturation variables, thermodynamic variables and the speed u. In our class of models, we assume that pressure variations are so small that they do not affect gas volume, which varies due to temperature or composition changes, see [11]. Thus the pressure is fixed and the main thermodynamic variables of the fluid phases are the temperature T and the compositions of each phase. We assume that the pores in the rock are fully filled with fluids (one of the fluids is gaseous). Different fluid phases do not mix microscopically. Each saturation variable in

the system is the fraction of the total volume of a fluid phase relative to the total volume of the fluid phases. If we denote the saturations by s_1, s_2, $\cdots$, s_p, where p is the number of immiscible phases, e.g., water, oil or gas, we know that, see [11]:

$$s_1 + s_2 + \cdots + s_p = 1. \tag{1.3}$$

Depending on its nature, a chemical species may exist in a single phase or it can coexist in matter several phases. The quantity of each chemical species that exists in each phase is described by concentration variables, which are denoted by c_{ij}, i.e., chemical species i in the phase j. In (1.1)-(1.2) there is an equation for each c_{ij}. The total concentration c_i of a chemical species is related to the concentrations per volume of this species in the phases in which it may exist by the following expression, see [11]:

$$c_i = c_{i1}s_1 + c_{i2} + \cdots c_{ip}s_p.$$

In general when there are p phases there exist $2^p - 1$ configurations.

In our notation, the number of balance equations that represents mass transfer is l. Equations in (1.1) represent the balance of each chemical species in different phases. Equations in (1.2) represent the conservation of chemical species existing in a single phase. The remaining $m - l + 1$ equations represent the conservation of chemical species existing in a single phase, where there is no mass transfer, as well as one equation for the total conservation of energy. The variables in the system are saturations variables, compositions of each phase, temperature T, which is the main unknown in the energy conservation equation and the Darcy speed u.

In the next section, we show that general compositional models are obtained from systems of form (1.1)-(1.2) by using asymptotic expansions around thermodynamic equilibrium (see also [4]).

As a representative example of the theory, we study a mathematical model for nitrogen and steam injection in a porous media. In this model, there appears a rarefaction evaporation wave; because it represents evaporation, this wave is not under thermodynamic equilibrium, so there is a source term. Rarefaction waves have straighten characteristics: this apparent contradiction is explained by noticing that the equilibrium system is the zero order approximation in the asymptotic expansion and the rarefaction evaporation is only a projection of this wave onto the phase configurations under thermodynamic equilibrium.

We give an example of a particular solution of (1.1)-(1.2), the Riemann solution, where the initial data is composed of two constant values, Eq. (6.1). The main motivation of our this model with this initial data is the clean up of sites with NAPL by using steam and nitrogen injection. However the theory can be used for models involving several phases and chemical species applied to improved oil recovery techniques.

2. The models

Systems of type (1.1)-(1.2) model thermal compositional flows in porous media. In such systems the pair $\mathcal{W} = (\mathcal{V}, u)$, with $\mathcal{V}$ lying in a domain in a m-dimensional space with m components is called *state variable*. $\mathcal{G}$ and $\mathcal{F}$ are the vector-valued functions of $m + 1$ components $\mathcal{G} = (\mathcal{G}_1, \mathcal{G}_2, \cdots, \mathcal{G}_{m+1})^T$ and $\mathcal{F} = (\mathcal{F}_1, \mathcal{F}_2, \cdots, \mathcal{F}_{m+1})^T$, whose domain is the set of variables $\mathcal{V}$. In (1.1)-(1.2) $u\mathcal{F}_i$ is the flux for the conserved quantity $\mathcal{G}_i$ and $\partial \mathcal{G}_i / \partial t$ is the corresponding accumulation term, for $i = 1, 2, \cdots m + 1$. On the right hand side there are the first l components of the source term vector $(\hat{q}_1, \hat{q}_2, \cdots, \hat{q}_l, 0, \cdots, 0)/\epsilon$, whose domain is the set $\mathcal{V}$. Physics dictates that the source terms are defined to vanish precisely for states

$\mathcal{V}$ in local thermodynamic equilibrium described by equations of state and thermodynamic constraints.

It is useful to rewrite the system (1.1)-(1.2) into equations for total conservation of each chemical species in all phases that are present. the type of phases present defines a phase configuration. For $j = 1, 2, \cdots, m - n$ and $i = m - n + 1, m - n + 2, \cdots, m + 1$ this new system can be written from (1.1)-(1.2) with a minimal number of source terms, for each configuration. This procedure is used in Petroleum Science, see [11], in order to minimize the number of balance equations in (1.1) and maximize the number of conservation laws in (1.2); thus we obtain for each configuration:

$$\frac{\partial}{\partial t} G_j(\mathcal{V}) + \frac{\partial}{\partial x} u F_j(\mathcal{V}) = q_j/\epsilon, \tag{2.1}$$

$$\frac{\partial}{\partial t} G_k(\mathcal{V}) + \frac{\partial}{\partial x} u F_k(\mathcal{V}) = 0, \tag{2.2}$$

with

$$G_j = (S\mathcal{G})_j, \quad F_j = (S\mathcal{F})_j, \quad G_k = (E\mathcal{G})_k \;\; and \quad F_k = (E\mathcal{F})_k,$$

where $\mathcal{G} = (\mathcal{G}_1, \cdots, \mathcal{G}_l, \mathcal{G}_{l+1}, \cdots, \mathcal{G}_{m+1})^T$ and $\mathcal{F} = (\mathcal{F}_1, \cdots, \mathcal{F}_l, \mathcal{F}_{l+1}, \cdots, \mathcal{F}_{m+1})^T$. The complementary matrices S and E are determined from the transfer terms between phases and the total conservation of each chemical species in each configuration.

For problems with important applications, local thermodynamic equilibrium is reached quickly, so the ϵ scale is very small (10^{-5} or less) and the source terms are large compared to the prevailing scale; thus it is useful to apply singular perturbation theory to the system (2.1)-(2.2). We assume that $\mathcal{V}$ and u can be expanded as:

$$\mathcal{V} = \mathcal{V}^0 + \epsilon \mathcal{V}^1 + \epsilon^2 \mathcal{V}^2 + \cdots, \tag{2.3}$$

$$u = u^0 + \epsilon u^1 + \epsilon^2 u^2 + \cdots. \tag{2.4}$$

Substituting (2.3) and (2.4) in (2.1)-(2.2) we have:

$$\frac{\partial}{\partial t} G_j(\mathcal{V}^0 + \epsilon \mathcal{V}^1 + \cdots) + \frac{\partial}{\partial x} \left(u^0 + \epsilon u^1 + \cdots\right) F_j(\mathcal{V}^0 + \epsilon \mathcal{V}^1 + \cdots) = q_j(\mathcal{V}^0 + \epsilon \mathcal{V}^1 + \cdots)/\epsilon,$$

$$\frac{\partial}{\partial t} G_k(\mathcal{V}^0 + \epsilon \mathcal{V}^1 + \epsilon^2 \mathcal{V}^2 + \cdots) + \frac{\partial}{\partial x} \left(u^0 + \epsilon u^1 + \cdots\right) F_k(\mathcal{V}^0 + \epsilon \mathcal{V}^1 + \epsilon^2 \mathcal{V}^2 + \cdots) = 0.$$

Multiplying the first equation by ϵ and setting $\epsilon = 0$ we obtain the lowest order approximation::

$$q_j(\mathcal{V}^0) = 0, \quad j = 1, 2, \cdots, m - n$$

$$\frac{\partial}{\partial t} G_i(\mathcal{V}^0) + \frac{\partial}{\partial t} u F_i(\mathcal{V}^0) = 0, \quad i = m - n + 1, m - n + 2, \cdots, m + 1. \tag{2.5}$$

Typically, the thermodynamic relationships and equations of state play a central role in multiphase models (2.1)-(2.2), which are represented here implicitly by $q_j(\mathcal{V}^0) = 0$. Each phase configuration is obtained by enforcing $q(\mathcal{V}^0) \equiv (q_1, q_2, \cdots, q_{n-m}) = 0$, where the local thermodynamic equilibrium is represented by relationships among the quantities $\mathcal{V}^0$. Since in this paper we are interested only in the problems with states at local thermodynamic equilibrium, which is formally the zero-order approximation, we drop the superscript zero from now on. We denote these variables as V and the respective state $W = (V, u)$. Note that V has a different meaning in different phase configuration.

Now the variables $\mathcal{V}$ are in equilibrium for each configuration, so, by extension of the notation, we indicate the dependence of the accumulation and the flux functions only on

the primary variables V, i.e., we use $G(V)$ and $F(V)$ representing $G(\mathcal{V})$ and $F(\mathcal{V})$ for a configuration, so the system (2.5) can be rewritten (in each phase configuration) in the unknowns $W = (V, u)$ as the compositional model:

$$\frac{\partial}{\partial t}G(V) + \frac{\partial}{\partial t}uF(V) = 0. \tag{2.6}$$

There are three groups of variables in the phase configuration, the basic variables V, or "primary variables" that are unknowns of (2.6). Notice that the system is "elliptic" in the variable u in the sense that perturbations in u propagate instantaneously; it turns out that u can be found from the primary variables and boundary conditions, so we call u a "secondary variable"; and the "trivial variables" are constant or they can be recovered from other variables in a simple way by relationships expressing local thermodynamic equilibrium in each configuration; they complement the variables in V.

3. The model for our example

We consider the one-dimensional horizontal flow resulting the injection of steam and nitrogen in a porous rock cylinder. The core consists of rock with constant porosity φ and absolute permeability k. We are interested in scales dictated by field reservoirs, we neglect the capillarity pressure and heat conductivity effects.

Darcy's law relates pressure gradient in each fluid phase with its seepage speed:

$$u_w = -\frac{kk_{rw}}{\mu_w}\frac{\partial p}{\partial x}, \qquad u_g = -\frac{kk_{rg}}{\mu_g}\frac{\partial p}{\partial x}, \tag{3.1}$$

where k is the absolute permeability of the rock, $k_{rw}(s_w)$ and $k_{rg}(s_g)$ are the relative permeabilities of water and gas, and μ_w, μ_g are their viscosities.

The fractional flow functions [11] for water and steam are given by:

$$f_w = \frac{k_{rw}/\mu_w}{k_{rw}/\mu_w + k_{rg}/\mu_g}, \qquad f_g = \frac{k_{rg}/\mu_g}{k_{rw}/\mu_w + k_{rg}/\mu_g}. \tag{3.2}$$

Using Darcy's law (3.1) and (3.2) we can write u_w and u_g as:

$$u_w = uf_w, \qquad u_g = uf_g, \quad \text{where} \quad u = u_w + u_g \tag{3.3}$$

is the *total* or *Darcy velocity*; s_w and s_g are the water and gas saturation.

4. The model equations

Using (3.3), we write the equations of mass balance for liquid water, gaseous steam and gaseous nitrogen as:

$$\frac{\partial}{\partial t}\varphi\rho_W s_w + \frac{\partial}{\partial x}uf_w\rho_W = +q_{g\longrightarrow a,w}, \tag{4.1}$$

$$\frac{\partial}{\partial t}\varphi\rho_{gw}s_g + \frac{\partial}{\partial x}uf_g\rho_{gw} = -q_{g\longrightarrow a,w}, \tag{4.2}$$

$$\frac{\partial}{\partial t}\varphi\rho_{gn}s_g + \frac{\partial}{\partial x}uf_g\rho_{gn} = 0, \tag{4.3}$$

where $q_{g\longrightarrow a,w}$ is the water mass source term (the condensation rate between of steam into water). The term $q_{g\longrightarrow a,w}$ is inferred from non-equilibrium thermodynamics [6]; this rate vanishes for states under thermodynamic equilibrium. ρ_W is the constant water density, ρ_{gw} (ρ_{gn}) denote the concentration of steam (nitrogen) in the gaseous phase (mass per unit gas

volume); in the presence of liquid water, thermodynamic considerations specify how these concentrations depend on temperature by Clausius Clapeyron and Raoult's laws, see [9].

The equation of energy conservation is based on an enthalpy formulation, see [1], [2], given by:

$$\frac{\partial}{\partial t}\varphi\left(\hat{H}_r + s_w H_W + s_g H_g\right) + \frac{\partial}{\partial x}\left(u f_w H_W + u f_g H_g\right) = 0. \tag{4.4}$$

Here $H_W = \rho_W h_W$, $H_g = \rho_{gw} h_{gW} + \rho_{gn} h_{gN}$, H_r is the rock enthalpy per unit volume and $\hat{H}_r = H_r/\varphi$; h_W, h_{gW} and h_{gN} are the enthalpies per unit mass of water in the liquid aqueous phase, of water in the gaseous phase and of nitrogen in the gaseous phase; these enthalpies depend on temperature, see [9].

5. Thermodynamic equilibrium condition

The system (4.1)-(4.4) is in the form (1.1)-(1.2). We can rewrite this system in a equivalent one by substituting Eq. (4.2) by the result of adding Eqs. (4.1) and (4.2):

$$\frac{\partial}{\partial t}\varphi\left(\rho_W s_w + \rho_{gw} s_g\right) + \frac{\partial}{\partial x}u\left(\rho_W f_w + \rho_{gw} f_g\right) = 0, \tag{5.1}$$

This new system is formed by a Eq. (4.1) representing the mass transfer of liquid water into gaseous water in the form (2.1), plus a subsystem formed by (5.1), (4.3) and (4.4), representing the conservation of total mass of water, nitrogen and conservation of energy, in the form ((2.2).

By enforcing the thermodynamic equilibrium laws, the system (4.1), (5.1), (4.3) and (4.4) reduces to systems of conservation laws for states satisfying $q_{g \longrightarrow a,w} = 0$, see Figure (5.1.a). This is the compositional model used in Petroleum Engineering for nitrogen and water, see [11].

The states under thermodynamic equilibrium laws determine three regions, which are called phase configurations: a two-phase configuration, tp, in which pores are filled with a mixture of liquid water, gaseous nitrogen and steam. In this case, the temperature is specified by the concentration of vapor in the gas through Clausius-Clapeyron; a single-phase gaseous configuration, spg, in which pores are filled with steam and nitrogen; a single-phase liquid configuration, spl, in which the pores contain only liquid water. Since each region is under thermodynamic equilibrium, we can use Gibbs' phase rule $f = c - p + 2$, where f represents the number of thermodynamic degrees of freedom, c of components and p of phases.

5.1. **Phase configurations.** In the tp configuration, there is only one thermodynamic variable, which is the temperature, since the pressure is fixed. The system to be solved is (5.1), (4.3) and (4.4) for the three unknowns temperature, saturation and total Darcy velocity.

In the spl configuration, there is only one thermodynamic variable, which is the temperature. System (5.1), (4.3) and (4.4) reduces to a single equation for the temperature.

The spg configuration deserve special attention because the unknowns have an interesting interpretation in this configuration. Since we fix the pressure, by Gibbs rule we have two other thermodynamic unknowns: temperature and gas composition. We need to rewrite the system (5.1), (4.3) and (4.4) by using the new unknown gas composition. To do so, we assume that nitrogen and steam in the gaseous phase behave as ideal gases with densities denoted by ρ_{gN} and ρ_{gW}, and that there are no volume effects due to mixing. Hence:

$$\rho_{gN} = \frac{M_N p_{atm}}{RT}, \quad \rho_{gW} = \frac{M_W p_{atm}}{RT}, \quad \frac{\rho_{gw}}{\rho_{gW}(T)} + \frac{\rho_{gn}}{\rho_{gN}(T)} = 1, \tag{5.2}$$
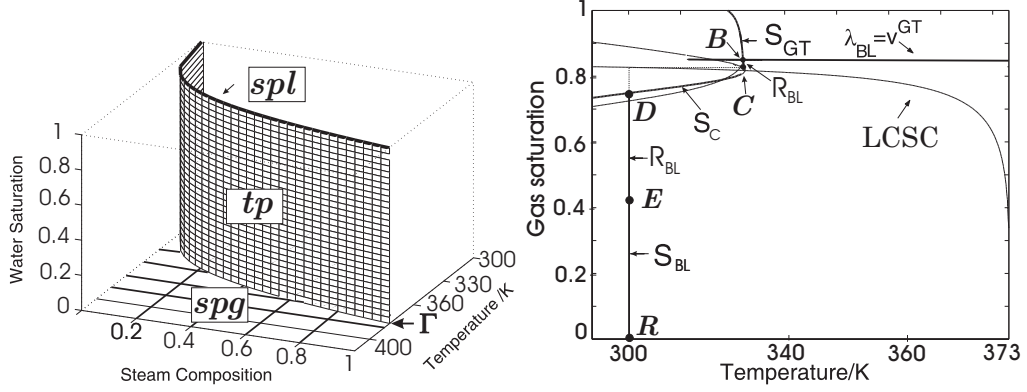
FIGURE 5.1. *a) Left:* Phase space for the phase configurations. *b) Right:* The states and wave sequences curves of the Riemann solution in the *tp* configuration.

where the p_{atm} is the pressure of the atmosphere, R is the gas constant; M_W, M_N are the nitrogen and water molar masses. From Eq. (5.2), we define the steam and nitrogen gas composition as:

$$\psi_{gw} = \rho_{gw}/\rho_{gW}(T) \qquad \text{and} \qquad \psi_{gn} = \rho_{gn}/\rho_{gN}(T), \quad \text{so} \quad \psi_{gw} + \psi_{gn} = 1. \qquad (5.3)$$

The compositions ρ_{gw} and ρ_{gn} are functions of temperature only, which can be obtained from (5.3.a) and (5.3.b). Using Eqs. (5.2.a), (5.2.b), (5.3.a) and (5.3.b), Eqs. (4.1)-(4.4) become:

$$\frac{\partial}{\partial t}\varphi\theta_W\psi_{gw}T^{-1} + \frac{\partial}{\partial x}u\theta_W\psi_{gw}T^{-1} = 0, \qquad (5.4)$$

$$\frac{\partial}{\partial t}\varphi\theta_N\psi_{gn}T^{-1} + \frac{\partial}{\partial x}u\theta_N\psi_{gn}T^{-1} = 0, \qquad (5.5)$$

$$\frac{\partial}{\partial t}\varphi\Big(\hat{H}_r + \psi_{gw}H_{gW} + \psi_{gn}H_{gN}\Big) + \frac{\partial}{\partial x}u\Big(\psi_{gw}H_{gW} + \psi_{gn}H_{gN}\Big) = 0; \qquad (5.6)$$

we have substituted ρ_{gW} and ρ_{gN} from Eqs. (5.2.a), (5.2.b), defined $H_{gW} = M_W p_{atm} h_{gW}/RT$ and $H_{gN} = M_N p_{atm} h_{gN}/RT$, where h_{gW} and h_{gN} are functions of T, see [9]. We have three variables to determine: temperature, gas composition and Darcy speed.

6. THE RIEMANN PROBLEM FOR STEAM AND NITROGEN INJECTION

We consider the injection of a mixture of steam and nitrogen in the *spg* below boiling temperature of pure water at prevailing pressure into a rock saturated with water. These initial data are typical for shallow subsurface clean up:

$$\begin{cases} (0, \psi_L, T_L, u_L) & \text{if } x = 0 \text{ (\textit{the injection point})}, \\ (1, \psi_{gw}(T_R), T_R, \cdot) & \text{if } x > 0. \end{cases} \qquad (6.1)$$

where $s = s_w$ is the water saturation and $\psi = \psi_{gw}$ is the steam composition. The speed u_L is specified at the injection side and the right side u_R is obtained from left and right states and the Riemann solution. The general solution of the Riemann problem associated to Eq. (2.5) consists of a sequence of elementary waves, namely shocks and rarefactions.

Shocks are special type of discontinuities appearing in solution of the Riemann problems. They need to satisfy the Rankine-Hugoniot conditions (RH), see [9], which can be written as:

$$v^s \left(G^+(V^+) - G^-(V^-) \right) = u^+ F^+(V^+) - u^- F^-(V^-), \tag{6.2}$$

where (V^+, u^+) is the state on the right of the shock and (V^-, u^-) is the state on the left of the shock; v^s is the shock speed; G^+ (G^-) and F^+ (F^-) are the accumulation and flux terms on the right (left) of the shock, which in general have different expressions in each phase configuration. We specify the left conditions for the variables V and u, but the right conditions are specified only for V. The speed u^+ is always obtained from the RH condition (6.2).

The smooth waves in the Riemann solution are obtained by differentiating all equations in (2.6) with respect to their variables obtaining a system of the form:

$$\left(B \frac{\partial}{\partial t} + A \frac{\partial}{\partial x} \right) (V, u)^T = 0,$$

where the matrices B and A are the derivatives of $G(V)$ and $uF(V)$ with respect to the variables V and u. $(V, u)^T$ represent a column vector. Since $G(V)$ does not depend on u, the last column in the matrix B is zero. The characteristic values λ and vectors $\vec{r}^i$, (where i is the label of each eigenvector) for the following system are the rarefaction wave speeds and directions:

$$A\vec{r}^i = \lambda B \vec{r}^i \quad \text{where } \lambda \text{ is obtained by solving} \quad det(A - \lambda B) = 0.$$

6.1. The fundamental waves.
In the *spg* configuration there are two waves: a thermal and a compositional wave. On the thermal wave, the temperature and speed u change while the gas composition is constant. The characteristic speed is denoted by λ_T. On the compositional wave, the gas composition changes while the temperature and speed are constant. This wave has speed denoted by λ_c.

In the *tp* configuration, there are two waves: an non-isothermal wave and a saturation isothermal (Buckley-Leverett) wave. The non-isothermal wave is composed by an evaporation rarefaction wave (denoted by R_e) and a condensation shock wave (denoted by S_c), where the saturation, temperature and speed change. The characteristic speed of R_e is denoted by λ_e and the shock speed of S_c is denoted by v_c. This wave is a projection of a non-equilibrium wave in another wave in the *tp* phase configurations under thermodynamic equilibrium.

On the saturation wave, the water saturation changes, but the temperature and speed are constant. The characteristic speed is denoted by λ^{BL} (Buckley-Leverett); this rarefaction wave is represented by R_{BL}. The shock is the Buckley-Leverett shock S_{BL} and its speed is denoted by v^{BL}.

There is only one wave connecting the *spg* and the *tp* configurations, which is also a condensation shock with speed v^{GT}; it is denoted by S_{GT}. This shock occurs in a thin region far away the thermodynamic equilibrium.

6.2. The Riemann solution for our example.
We consider the Riemann problem with left and right states in the form (6.1): L has $\psi_L = 0.1$, $T_L = 340K$ and R has $T_R = 300K$.

Since L is in the *spg* configuration, see Fig. 5.1, we propose a shock on the S_{GT}; this shock connects L to an intermediate state E_1. The speed of this shock satisfies $v^{GB}(L; E_1) = \lambda^{BL}(E_1)$, where λ^{BL} is the Buckley-Leverett speed. The state E_1 is obtained by intersecting

the Rankine-Hugoniot curve S_{BL} from L with the curve where v^{BL} and λ^{BL} coincide. We can verify that $v^{GB}(L; E_1) < \lambda_T(L)$.

From E_1 there exists an isothermal rarefaction R^{BL} up to E_2, with fixed temperature T_{E_1}. The state E_2 is obtained using the "left-characteristic shock curve" (*lcsh*, see Fig. (5.1.*b*)).

The *lcsh* curve (see Fig. (5.1.*b*)) is formed by the states P_1 on the R^{BL} (from E_1), such that there is a state P_2 belonging to the condensation shock S_c (from P_1) and to the vertical line from the right state R, where the equality $v_c(P_1; P_2) = \lambda^{BL}(P_1)$ is satisfied. The vertical line represents an isothermal Buckley-Leverett shock and a rarefaction curve.

The state E_2 is the intersection between the vertical line starting at the right state R and the "left characteristic shock curve", see Figure (5.1.*b*). The state E_3 is the intersection between S_c starting at E_2 and the vertical line from the right state R. From E_3 there is an isothermal rarefaction up to E_4. The state E_4 is obtained so as to satisfy the equality $\lambda^{BL}(E_4) = v^{BL}(E_4; R)$. The solution is summarized in the Figures (5.1.*b*) and (6.1).

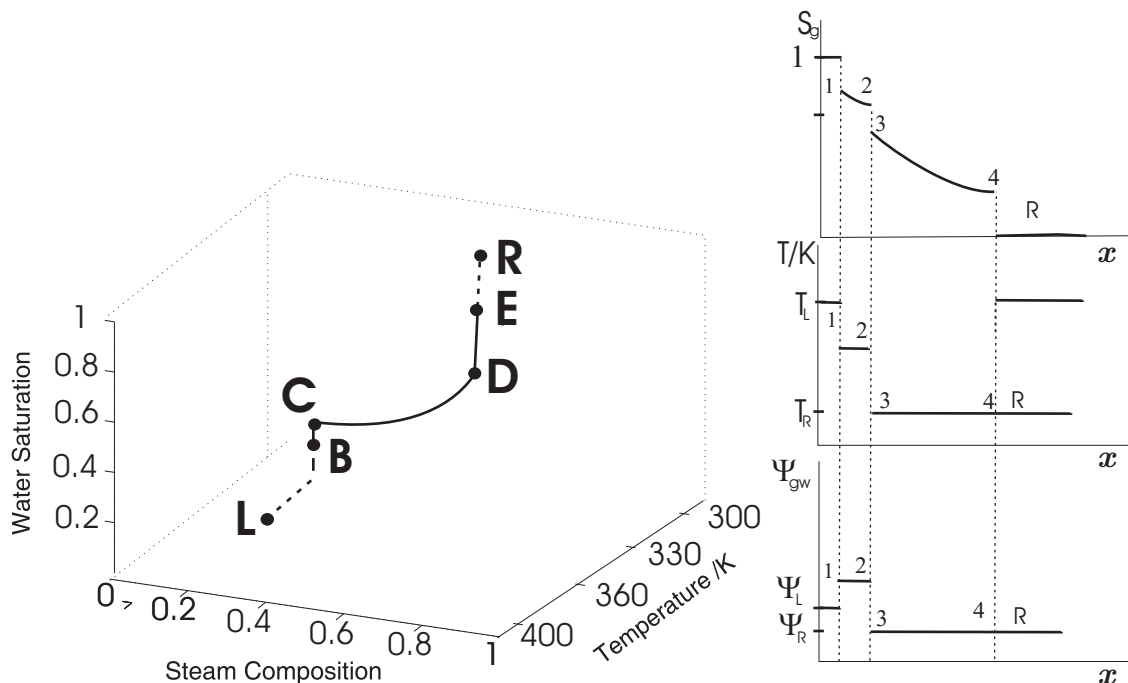Condensation of water occurs in the shocks S_{GT} and S_c between the states L-E_1 and E_2-E_3.

FIGURE 6.1. *a) Left:* Riemann solution in phase space V, for our example. In the Riemann solution, we have removed the surface in the phase space of Fig. 5.1. *b) Right:* The saturation, temperature and gas composition profiles for some $t > 0$. In both Figures, the numbers 1 to 4 indicate the intermediate states E_1 to E_4.

7. SUMMARY AND CONCLUSIONS

By asymptotic expansions, we have found a systematic procedure to reduce balance laws including mass transfer between phases to a local thermodynamic equilibrium compositional model. The method has been applied to non-isothermal flow.

We have also shown an example of the Riemann solution for the injection of a mixture of nitrogen and steam into a porous rock filled with water and sketched a systematic theory for the Riemann solution. This solution shows that in principle it is possible to clean up NAPL's from the soil with a mixture of nitrogen and steam at moderate temperatures, $(67^{o}C)$. The set of solutions depends continuously on the Riemann data. For other cases, see [9].

Table 2, Summary of physical input parameters and variables			
Physical quantity	*Symbol*	*Value*	*Unit*
Water, steam fractional functions	$f_w,\ f_g$	Eq. (3.2) .	$[\mathrm{m}^3/\mathrm{m}^3]$
Porous rock permeability	k	1.0×10^{-12}.	$[\mathrm{m}^3]$
Water, steam relative permeabilities	$k_{rw},\ k_{rg}$	see [9] for equations	$[\mathrm{m}^3/\mathrm{m}^3]$
Pressure	p_{atm}	1.0135×10^5.	$[\mathrm{Pa}]$
Water, gaseous phase velocity	$u_w,\ u_g$	Eq. (3.1) .	$[\mathrm{m}^3/(\mathrm{m}^2\mathrm{s})]$
Total Darcy velocity	u	$u_w + u_g$, Eq. (3.3) .	$[\mathrm{m}^3/(\mathrm{m}^2\mathrm{s})]$
Rock and water heat capacities	C_r and C_W	2.029×10^6 and 4.018×10^6.	$[\mathrm{J}/(\mathrm{m}^3\ \mathrm{K})]$
Steam and nitrogen enthalpies	$H_{gW},\ H_{gN}$	see [9] for equations	$[\mathrm{J}/\mathrm{m}^3]$
Water and Rock enthalpies	$H_W,\quad H_r$	see [9] for equations	$[\mathrm{J}/\mathrm{m}^3]$
Water, steam saturations	$s_w,\ s_g$	Dependent variables.	$[\mathrm{m}^3/\mathrm{m}^3]$
Temperature, Reference Temperature	$T\quad T_{ref}$	Dependent variable, $293K$.	$[\mathrm{K}]$
Water, gaseous phase viscosity	$\mu_w,\ \mu_g$	see [9] for equations	$[\mathrm{Pa\ s}]$
Steam and nitrogen densities	$\rho_{gw},\ \rho_{gn}$	see [9] for equations	$[\mathrm{kg}/\mathrm{m}^3]$
Constant water density	ρ_W	998.2.	$[\mathrm{kg}/\mathrm{m}^3]$
Steam and nitrogen gas composition	$\psi_{gw},\ \psi_{gn}$	Dependent variables.	$[-]$
Universal gas constant	R	8.31	$[J/mol/K]$
Nitrogen and water molar masses	$M_N,\ M_W$	0.28, 0.18	$[kg/mol]$
Rock porosity	φ	0.38.	$[\mathrm{m}^3/\mathrm{m}^3]$

REFERENCES

[1] BEEK, W. J. AND MUTZALL, M. K. *Transport Phenomena*, John Willey and Sons.

[2] BIRD, R. B., STEWART, W. E., AND LIGHFOOT, E. N., *Transport Phenomena*, John Wiley and Sons (1960).

[3] BRUINING, J., MARCHESIN, D., *Nitrogen and steam injection in a porous medium with water*, Transport in Porous Media, Vol. 62, 3, (2006), pp. 251-281.

[4] BRUINING, J.AND DUIJN, C.J., *Traveling waves in a finite condensation rate model for steam injection*, Computational Geosciences, Vol. 10, 4 , (2006), pp. 373-387.

[5] HIRASAKI, G. *Application of the theory of multicomponent multiphase displacement to three component, two-phase surfactant flooding*, SPEJ, (Apr. 1981), pp. 191-204.

[6] D. JOU, J. CASAS-VASQUEZ, AND G. LEBON. *Extended Irreversible Thermodynamics*. Springer- Verlag, Heidelberg, 2001.

[7] LAMBERT, W., *Doctoral thesis: Riemann solution of balance systems with phase change for thermal flow in porous media*, IMPA, available at www.preprint.impa.br, 2006.

[8] LAMBERT, W., MARCHESIN, D. AND BRUINING, J., *The Riemann Solution of the balance equations for steam and water flow in a porous medium*, Methods of Analysis and Applications, (12), (2005), pp. 325-348.

[9] LAMBERT, W., MARCHESIN, D., *The Riemann solution for the nitrogen and steam injection with applications in groundwater recovery*, IMPA, available at www.preprint.impa.br.

[10] LAMBERT, W., MARCHESIN, D., *Singular perturbation for rarefaction waves in balance laws with relaxation*, in preparation.

[11] LAKE, L. W., *Enhanced Oil Recovery*, Prentice Hall, 1989.

[12] POPE, G.A., AND NELSON, R. C., *A chemical flooding compositional simulator*, SPEJ, (Oct. 1978), pp. 339-354.