

Saturation waves and chemical transport in two phase flows

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Abstract

The equations describing the vertical transport of mass, energy and unreacting chemicals in a two phase reservoir are analysed when capillarity can be ignored. The singular system of equations comprises of a mixed system of diffusive and wave equations. Simplified analyses show the existence of continuous flux vectors, and shock transport by contact discontinuities. Steady flows are shown to allow for more than two (vapour and liquid dominated) saturations for a given mass, energy and chemical flux. The additional possible saturations resulting from the presence of the chemicals are associated with the possible existence of narrow regions of high conductive heat flux driven by rapid changes in the partial pressure of the corresponding chemical. However, when thermal conduction and chemical diffusion are unimportant, then only the vapour and liquid dominated cases appear likely to occur.

1 INTRODUCTION

Two phase conditions occur in liquid dominated geothermal fields when the pressure on rising hot water reduces sufficiently for boiling to begin. Such two phase conditions can exist for several hundred metres in vertical height (Allis and Hunt, 1986), and are recognised from the pressure closely approximating estimates for the saturation temperature for the chemical composition of the geothermal fluid.

Two types of two phase reservoir are known (Grant et al., 1982): liquid and vapour dominated reservoirs, in which the enthalpy of the produced geothermal fluid is close to that for water or steam, respectively. There is no widely accepted reason as to why one geothermal field is either liquid or vapour dominated (Straus and Schubert, 1981). However, the equations of steady flow of mass and energy in two phase conditions can allow two saturations to exist for certain mass and energy flows, and this redundancy may be related in some way to the two types of two phase reservoirs observed.

The aim of this paper is to show that the presence of (non-reacting) chemicals in the rising geothermal fluid can allow even more redundancy in the allowable saturation states corresponding to certain mass, energy and chemical fluxes. We suggest that for each new possible saturation there is a new possible mechanism of energy transport in two phase conditions, and a possible new boundary layer phenomena associated with the corresponding chemical.

A key assumption in this paper is that capillarity effects are negligible. Because of the large density difference between water and steam, the height of the capillarity fringe in two phase conditions is perhaps of the order of one metre. Since this height scale is small relative to those usually encountered in geothermal modelling, capillarity is usually ignored, and we shall also make that assumption below.

2 MATHEMATICAL FORMULATION

The equations for mass, energy and chemical conservation in a two phase porous medium can be written as

$$\frac{\partial \rho_i}{\partial t} + \frac{\partial J_i}{\partial z} = 0 \quad (1)$$

where ρ_i is a conserved density, J_i is the corresponding flux of conserved quantity and we allow only vertical transport. Here the index i represents mass, energy and chemical species, $i = M, E, X^m$ for $m = 1, n$, and

$$\begin{aligned} \rho_M &= \phi \rho_l S + \phi \rho_v (1 - S) \\ \rho_E &= (1 - \phi) \rho_R U_R + \phi \rho_l U_l S + \phi \rho_v U_v (1 - S) \\ \rho_{X_i} &= \phi \rho_l X_l^m S + \phi \rho_v X_v^m (1 - S) \end{aligned} \quad (2)$$

and

$$\begin{aligned} J_M &= \rho_l V_l + \rho_v V_v \\ J_E &= \rho_l h_l V_l + \rho_v h_v V_v - K \frac{\partial T}{\partial z} \\ J_{X^m} &= \rho_l X_l^m V_l + \rho_v X_v^m V_v - D_l^m \frac{\partial X_l^m}{\partial z} - D_v^m \frac{\partial X_v^m}{\partial z} \end{aligned} \quad (3)$$

where

$$V_l = -\frac{k k_l}{\mu_l} (\nabla P - \rho_l g) \quad (4a)$$

$$V_v = -\frac{k k_v}{\mu_v} (\nabla P - \rho_v g) \quad (4b)$$

are the corresponding Darcy liquid and vapour fluxes.

In (1) to (4b), ϕ is porosity; ρ_l , ρ_v and ρ_R are liquid, vapour and rock density; S saturation; t time; z the vertically downward coordinate; U_R , U_l and U_v are internal energy of rock, liquid and vapour; X_l^m , X_v^m are liquid and vapour mass fractions of chemical component m ; h_l and h_v are liquid and vapour enthalpy; K thermal conductivity; T temperature; V_l and V_v are liquid and vapour volumetric fluxes; D_l^m , D_v^m are diffusivity coefficients for component m in the liquid and vapour, both of which may depend on relative permeabilities, densities, tortuosity, porosity, etc; k is permeability; k_l and k_v are liquid and vapour relative permeability; μ_l and μ_v are liquid and vapour viscosity; P pressure and g is gravitational acceleration. The relative permeability functions k_l and k_v are assumed to be functions of saturation alone.

Not all of the variables above are independent. In a two phase region, the mole fraction of component m in the vapour is proportional to the corresponding mole fraction in the liquid, according to Henry's Law. Hence X_v^m can be considered to be a function of X_l^m , $X_v^m = X_v^m(X_l^m)$. In the following development we shall assume that both X_v^m and X_l^m can be described as functions of the partial pressures, P_m , of each chemical component.

Further, we shall assume local thermodynamic equilibrium, and so temperature can be considered a function of the total pressure, and of the partial pressures of the chemical components. We can therefore write

$$T = T(P, P_m) \quad (5)$$

The dependent variables in our two phase system are then P , S and P_m . Specifically, if n is the number of chemical species, then there are $n+2$ conservation equations, and $n+2$ dependent variables. Alternatively, if we are describing a single phase system, then we have set S either to zero or unity, but now T is also a dependent variable, along with P and P_m . Since we have the same number of equations as dependent variables, we shall proceed by assuming that the equations above are closed and solvable.

Finally, if some of the variables are discontinuous, then the corresponding shock speed is determined from the Rankine-Hugoniot conditions. Let $\Delta()$ represent the jump in a physical variable $()$ at a shock, when traversing the shock in a fixed direction. Then conservation of mass, energy and chemical species requires

$$\Delta J_i = b \Delta \rho_i \quad i = M, E, X^m \quad (6)$$

where b denotes the shock velocity.

3 INFINITESIMAL SHOCKS

We show in this section that for infinitesimal shocks there always exists a continuous flux vector, and that some variables are transported diffusively, whereas others are transported as waves. From the Rankine-Hugoniot equations, we can write

$$\Delta \rho_i = \frac{\partial \rho_i}{\partial S} \Delta S + \frac{\partial \rho_i}{\partial P_m} \Delta P_m \quad (7)$$

since pressure is continuous across a shock. Consequently, for infinitesimal shocks, we can write the Rankine Hugoniot equations as

$$\left[\frac{\partial \rho_i}{\partial S} \frac{\partial \rho_i}{\partial P_m} \right] \begin{bmatrix} \Delta S \\ \Delta P_m \end{bmatrix} = \frac{\Delta J_i}{U} \quad (8)$$

where U is the shock speed. Equations (8) are $n+2$ equations for the $n+1$ variables ΔS and ΔP_m , and so the determinant of the associated augmented matrix must be zero,

$$\det \left[\frac{\partial \rho_i}{\partial S} \frac{\partial \rho_i}{\partial P_m} \Delta J_i \right] = 0 \quad (9)$$

Expanding (9) down the $n+2$ column yields a linear sum of ΔJ_i terms equalling zero. However, since the partial derivative terms in (9) are assumed constant for infinitesimal shocks, these terms can be taken inside the Δ arguments, which yields a continuous flux vector (since its change across the shock is zero).

If now some of the chemicals are assumed to be diffusive, then these chemicals, as well as pressure will be continuous across a shock. If we assume that N of the variables (pressure and $N-1$ chemicals) are diffusive (continuous at a shock), then proceeding as above yields an $(n+2, n+3-N)$ augmented matrix of rank $n+2-N$. Hence we can select N square $(n+3-N, n+3-N)$ submatrices from the augmented matrix, and these N submatrices must be singular. Then expanding out the corresponding N determinants yields N continuous flux vectors, as above, since a particular ΔJ_i appears linearly in each term in each determinant, and the corresponding coefficients can be taken inside the Δ argument.

Alternatively, if N of the variables are continuous,

$$J_i = J_i(P, S, X^m, \nabla \zeta) \quad (10)$$

where ζ comprises the set of N dependent variables which are diffusive. In general, P will belong to ζ , and so may other dependent variables for which diffusion, for example, in the vapour phase is important. We shall assume that the continuous variables ζ are linearly independent. For example, if we had chosen temperature as one dependent variable, instead of pressure, then the conserved fluxes are likely to depend on spatial gradients of all of the chemicals. If several of these chemicals were non-diffusive, then linear dependencies would hold in the spatial derivatives in (10).

If the remaining $n+2-N$ non-diffusive dependent variables are denoted by θ , then

$$(\zeta \cup \theta) = (P, S, P_m) = (\eta) \quad (11)$$

where η denotes all of the dependent variables.

The time derivatives of densities in the conservation equations can now be expanded out in terms of time derivatives of the η terms, the matrix $\frac{\partial \rho}{\partial \eta}$ inverted, and η set equal to ζ , to yield

$$\frac{\partial \zeta}{\partial t} + \frac{\partial}{\partial z} \left(\frac{\partial \zeta}{\partial \rho} J \right) = 0 \quad (12)$$

since for infinitesimal shocks, the matrix $\frac{\partial \zeta}{\partial \rho}$ is constant. Since ζ is continuous, the flux vectors J_c are continuous

$$J_c = \frac{\partial \zeta}{\partial \rho} J \quad (13)$$

and so for each continuous variable, ζ , there corresponds a continuous flux vector. In (13), J_c denotes N continuous flux vectors.

Note from (9), the column vectors $\frac{\partial \rho}{\partial \theta}$ span the column vector ΔJ , since the matrix in (9) has rank $n+2-N$. But as the column vectors $\frac{\partial \zeta}{\partial \rho}$ and $\frac{\partial \rho}{\partial \theta}$ are orthogonal, then the column vectors ΔJ and $\frac{\partial \zeta}{\partial \rho}$ are orthogonal. This is just the condition that J_c defined in (13) are continuous.

To proceed we shall introduce a canonical notation. Our canonical choice is that for each discontinuous or continuous variable, belonging to either θ or ζ , we associate a corresponding density and flux according to

$$\zeta = (P, \dots) = (E, \dots) \quad (14a)$$

$$\theta = (S, \dots) = (M, \dots) \quad (14b)$$

That is, we associate energy with pressure, mass with liquid saturation, and each conserved chemical with the corresponding partial pressure of chemical in the liquid. In this way, we can group densities and fluxes into $\rho_\zeta, \rho_\theta, J_\zeta, J_\theta$, depending on the importance of the corresponding diffusivity for each dependent variable.

We shall also assume that gradients of the N continuous variables, $\nabla\zeta$ can be replaced by the corresponding N continuous flux vectors,

$$\nabla\zeta = \nabla\zeta(\zeta, \theta, J_c) \quad (15)$$

and so the corresponding conserved fluxes J can be written

$$J = J(\zeta, \theta, J_c) \quad (16)$$

Expanding out the θ conservation laws, using our canonical classification above, then yields

$$\frac{\partial\theta}{\partial t} + c\nabla\theta = \frac{\partial\theta}{\partial\rho_\theta} \left[\left(\frac{\partial J_\theta}{\partial J_c} - \frac{\partial\rho_\theta}{\partial\zeta} \right) \frac{\partial\zeta}{\partial t} - \frac{\partial J_\theta}{\partial\zeta} \nabla\zeta \right] \quad (17)$$

where the square characteristic matrix c of order $n+2-N$ by $n+2-N$ is the Jacobian matrix

$$c = \frac{\partial J_\theta}{\partial\rho_\theta} \quad (18)$$

The eigenvalues of (18) are then the characteristic speeds for the wave equations in (17).

Finally, from (12), the diffusive equations for infinitesimally small shocks are

$$\frac{\partial\zeta}{\partial t} = D\nabla^2\zeta - \frac{\partial J_c}{\partial\zeta} \nabla\theta - \frac{\partial J_c}{\partial\theta} \nabla\theta \quad (19)$$

where the diffusivity matrix D in (19) satisfies

$$D = -\frac{\partial J_c}{\partial\nabla\zeta} = -\frac{\partial J}{\partial\nabla\zeta} \frac{\partial\zeta}{\partial\rho} \quad (20)$$

A general analysis of the diffusivity matrix in two phase conditions has been completed by Weir (1995).

4 CONTACT DISCONTINUITIES

The previous section showed that with infinitesimal shocks a continuous flux vector always exists. This is a surprising result, since if the vapour and liquid diffusivities, and thermal conductivity are ignored, then there are no diffusive processes in the system which will smooth out initially steep gradients, and so some discontinuous behaviour is then expected. Despite this, we always have at least one continuous flux vector.

This section shows that a continuous flux vector also occurs for some two phase systems containing chemicals, for finite shocks. (A similar result is well known for the isothermal Polymer Flood model; we are allowing here nonisothermal behaviour and chemicals being present in both liquid and vapour phases). Motivated by the Buckley-Leverett assumptions of constant liquid and vapour density, we shall assume in this section that ρ_l, ρ_v, h_l, h_v are constant, and that U_R is a function of pressure alone. We shall further assume that the ratio of vapour to liquid mass fractions for a given chemical is constant.

The equations to be considered in this section are therefore

$$\begin{aligned} \phi(\rho_l - \rho_v) \frac{\partial S}{\partial t} + \frac{\partial J_M}{\partial z} &= 0 \\ (1 - \phi) \rho_R \frac{dU_R}{dP} \frac{\partial P}{\partial t} + \phi(\rho_l h_l - \rho_v h_v) \frac{\partial S}{\partial t} + \frac{\partial J_E}{\partial z} &= 0 \\ \phi \rho_l \frac{\partial(SX_l^m)}{\partial t} + \phi \rho_v \frac{\partial[(1-S)X_v^m]}{\partial t} + \frac{\partial J_X^m}{\partial z} &= 0 \end{aligned} \quad (21)$$

Eliminating the time derivatives of saturation between equations (21) yields the pressure equation

$$(\rho_l - \rho_v)(1 - \phi) \rho_R \frac{dU_R}{dP} \frac{\partial P}{\partial t} + \rho_l \rho_v (h_v - h_l) \frac{\partial(V_l + V_v)}{\partial z} = 0 \quad (22)$$

Here V_l and V_v are the liquid and vapour volumetric fluxes, and since we are ignoring conduction and diffusion

$$\begin{aligned} J_M &= \rho_l V_l + \rho_v V_v \\ J_E &= \rho_l h_l V_l + \rho_v h_v V_v \\ J_X^m &= \rho_l X_l^m V_l + \rho_v X_v^m V_v \end{aligned} \quad (23)$$

Eliminating the time derivatives of saturation between equations (21), and using (22), yields the chemical wave equations

$$\frac{\partial X_l^m}{\partial t} + c_X^m \frac{\partial X_l^m}{\partial z} = -\frac{(1 - a^m) X_l^m (1 - \phi) \rho_R \frac{dU_R}{dP} \frac{\partial P}{\partial t}}{\phi(h_v - h_l)[\rho_l S + \rho_v(1 - S)]} \quad (24)$$

where c_X^m is the wave speed for chemical m ,

$$c_X^m = \frac{\rho_l V_l + a^m \rho_v V_v}{\phi[\rho_l S + a^m \rho_v(1 - S)]} \quad (25)$$

$$X_v^m = a^m X_l^m \quad (26)$$

and a^m is assumed to be constant for each chemical.

The wavespeed in (25) generalises the wavespeed in the Polymer Flood model, which assumes chemicals are restricted to the liquid phase only, or that a^m is zero. It is surprising that the chemical wave equation, (24), is derivable without any requirement on the form of the liquid and volumetric fluxes, V_l and V_v . If the pressure is essentially steady, then (24) shows that the chemical liquid mass fractions X_l^m are translated with speed c_X^m .

The corresponding wave equation for saturation does depend on the form of the volumetric fluxes. We shall assume that the mass flux J_M can be expressed as a function of the volumetric flux vector, J_c ,

$$J_c = V_l + V_v \quad (27)$$

and of saturation

$$J_M = J_M(S, J_c) \quad (28)$$

which, when substituted into (21), yields

$$\frac{\partial S}{\partial t} + c_M \frac{\partial S}{\partial z} = -\frac{\frac{\partial J_M}{\partial J_c} (1 - \phi) \rho_R \frac{dU_R}{dP} \frac{\partial P}{\partial t}}{\phi} \quad (29)$$

where

$$c_M = \frac{1}{\phi} \frac{\partial V_l}{\partial S} \quad (30)$$

We shall show below that c_M and c_X^m are the corresponding characteristic speeds for saturation and chemicals. If a shock occurs then the Rankine-Hugoniot equations hold, ie,

$$\begin{aligned} \phi b &= \frac{\rho_l \Delta V_l + \rho_v \Delta V_v}{(\rho_l - \rho_v) \Delta S} \\ &= \frac{\rho_l h_l \Delta V_l + \rho_v h_v \Delta V_v}{(\rho_l h_l - \rho_v h_v) \Delta S} \\ &= \frac{\rho_l \Delta(X_l^m V_l) + \rho_v \Delta(X_v^m V_v)}{\Delta[\rho_l X_l^m S + \rho_v X_v^m (1 - S)]} \end{aligned} \quad (31)$$

From the second and third terms in (31), $\Delta(V_l + V_v)$ is zero, which is equivalent to J_e being continuous. Then from the first and second terms in (31), if there is a discontinuous jump in saturation, it must move with speed b satisfying

$$b = \frac{\Delta V_l}{\phi} \quad (32)$$

From the first and fourth terms in (31),

$$\begin{aligned} \phi b &= \frac{\rho_l \Delta(X_l^m V_l) + \rho_v \Delta(X_v^m V_v)}{\Delta[\rho_l X_l^m S + \rho_v X_v^m (1 - S)]} \\ &= \frac{(X_l^m)^+ N^+ - (X_l^m)^- N^-}{(X_l^m)^+ D^+ - (X_l^m)^- D^-} \end{aligned} \quad (33)$$

where N^+ , N^- , D^+ , D^- are defined within (33). Rearranging (33) shows that $X_l^m(D\phi b - N)$ is continuous. But from (32), $(D\phi b - N)$ is also continuous. Consequently, if there is a jump in values of X_l^m , then $D\phi b - N$ is zero. Hence the speed of any discontinuity in X_l^m is then $N/\phi/D$, which from (25) equals c_X^m , or

$$b = c_X^m \quad (34)$$

is the second set of solutions to (31), and since these shock speeds differ from that in (32), saturation is continuous where there is a jump in X_l^m . An alternative interpretation of (34) is that if J_X/ρ_X is continuous, then the corresponding Rankine-Hugoniot equation is satisfied, and J_X/ρ_X is the shock speed. It remains to calculate the characteristics for the system of equations in (21).

Since the characteristics equal the shock speeds in the limit of infinitesimal shocks in S and X_l^m , the characteristic for saturation from (32) equals the Buckley Leverett expression, ie, $\frac{\partial V_l}{\partial S}/\phi$, where the partial derivative is taken keeping J_e , P and X_l^m constant. The characteristics for chemical concentrations X_l^m from (34) equals the corresponding shock and wave speed, c_X^m . The shocks in chemical concentration then are contact discontinuities, since these shock and characteristic speeds are equal.

5 STEADY FLOWS

In steady vertical flows, the fluxes J_i are constant. Suppose we prescribe constant vertical mass, energy and chemical fluxes, J_M^0 , J_E^0 and $J_{X_i}^0$. Then there are $n + 2$ ordinary differential equations,

$$J_i^0 = a_i^0 \frac{dP}{dz} + \sum_{m=1}^n b_{im}^0 \frac{dX_m^m}{dz} + c_i^0 \quad (35)$$

among the $n + 1$ spatial gradients, where the steady coefficients a_i^0 , b_{im}^0 and c_i^0 are functions of P , S and P_m . Since the $n + 2$ system of equations in (35) are overdetermined, the square $n + 2$ by $n + 2$ augmented matrix for (35) must be singular, ie,

$$\det[a_i^0, b_{im}^0, c_i^0 - J_i^0] = 0 \quad (36)$$

Considering (36) as an equation for liquid saturation, S , then from (3) to (4b), (36) is an algebraic equation of degree n in S (from the vapour diffusion terms), and degree $n + 2$ in k_l and k_v (since each row and column entry is linear in k_l and k_v). The number of solutions for S then depends on the behaviour of the relative permeability functions. In particular, if k_l and k_v sum to unity, and k_l is a linear function of saturation, then there are at most $n + 2$ possible saturations satisfying (36).

In the case of pure two phase water substance, it is well known that there are at most two steady saturations possible for a given mass and energy flux - the liquid and vapour dominated cases. (These two possibilities only occur when the calculated values for liquid saturation are real and positive, which restricts the possible values of pressure and mass and energy fluxes allowed in a two phase region. Analogous restrictions must also hold for two phase conditions to occur in the presence of chemical fluxes.) That other states are also possible (in principle) from (36) when chemicals are present relies completely on the diffusion of the chemicals via the vapour and liquid diffusivity and the thermal conductivity terms, through b_{im}^0 in (36). Since the role of these diffusive terms may be relatively small in many instances, it is worth enquiring of the consequences when they are set to zero.

Then (36) reduces to

$$\text{rank}[a_i^0, c_i^0 - J_i^0] = 1 \quad a = 1, n + 2 \quad (37)$$

From the first two rows of the matrix in (37), we see that there are at most two (two phase) saturations, provided k_l and k_v sum to unity, and k_l is a linear function of saturation. Selecting one of these saturations, and considering the other rank 1 matrices in (37), we obtain an equation for each chemical present. The number of solutions for each P_m then depends on the importances of liquid and vapour density, enthalpy and diffusivities on P_m , and if such dependence is weak, then there is essentially a linear equation to be solved for each value of P_m . Hence we conclude that when chemical and thermal diffusion are unimportant, then there are probably only two solutions at most to (37).

Having obtained the allowable saturations from either (36) or (37), then saturation can be eliminated from (35), and the ordinary differential equations for P and (perhaps) P_m can be integrated. Integration proceeds as long as the coefficient matrix of the derivatives is nonsingular :

$$\text{rank}[a_i^0, b_{im}^0] = n + 1 \quad (38)$$

If (38) fails, then large spatial derivatives will occur from (35). Since large spatial derivatives are not expected to occur from the pressure terms, we expect approximately shock-like behaviour to occur for some of the chemical species when (38) fails.

Examples of a given steady flux of mass, energy and carbon dioxide which allow three saturations to occur in the vertical transport of a **two-phase H_2O-CO_2 system** (Takenouchi and Kennedy, 1964) have been obtained by Weir and Kissling (1995). This analysis showed the new saturations are associated with regions of high conductive energy transport, driven by large gradients in the partial pressure of carbon dioxide. However, when diffusion and thermal conductivity are ignored, multiple saturations do not occur (Sutton and McNabb, 1977).

6 BOUNDARY LAYERS

Since the role of chemical diffusion and thermal conductivity on transport is usually small in two phase conditions, relative to effects from liquid and vapour convection, we do not anticipate such terms being important over large vertical distances. However, it is possible that one chemical can change its partial pressure rapidly over a narrow vertical zone, perhaps due to an effective phase change occurring for that chemical.

A zone of rapidly changing partial pressure can imply a zone of rapidly changing temperature, from (5). Thus increased conductive energy fluxes can occur in these boundary layer zones, since

$$J_E = J_l + J_v - K \left(\frac{\partial T}{\partial P} \nabla P + \frac{\partial T}{\partial P_m} \nabla P_m \right) \quad (39)$$

where J_l and J_v are the convected liquid and vapour energy fluxes. Consequently, if in the narrow zone of rapidly changing partial pressure a large fraction of the energy transport is through conduction (assuming P will not change dramatically here), then the vertical length scale Z_m associated with the rapidly varying partial pressure is

$$Z_m = \frac{K \frac{dT_s}{dP_{H_2O}} \Delta P_m}{J_E} \quad (40)$$

where ΔP_m is the change in pressure across the boundary layer zone, and we have assumed that to first order the temperature of water is close to the saturation temperature of pure water for that pressure. If we assume that the pressure change ΔP_m is of the same order as the saturation pressure of pure water, and that the saturation pressure of pure water varies as the fourth power of temperature, then we can simplify (40) to

$$Z_m \sim \frac{KT_s}{4J_E} \sim \frac{50}{J_E} \quad (41)$$

in SI units. Consequently, energy fluxes of order ten (ten watts per square metre), or less, are needed before we expect to observe such boundary layer zones.

7 CONCLUSIONS

- Equations of unreacting chemical transport have been analysed in a two phase reservoir;
- Both shock-like and diffusive behaviour occurs;
- Continuous flux vectors can exist in the presence of shocks;
- Shocks can transport as contact discontinuities;
- When chemicals are distributed in both phases, saturations additional to the well-known liquid and vapour dominated states are possible;

- Each new saturation state appears to be associated with the possibility of enhanced conductive energy flux, probably over boundary layer zones;
- Not all of the possible saturation states arise in the geothermal context, but some of these new states may produce numerical instabilities;
- Examples of such boundary layer or transition zones arise in the numerical simulation of vertical transport of H_2O and CO_2 by McKibbin and Pruess (1988), OSullivan et al (1985), and White (1995).

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