Thermodynamic Analysis of Relaxation Model for Non-Equilibrium Phase Behavior of Hydrocarbon Mixtures

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Abstract. Mathematical models of phase behavior are widely used to describe multiphase oil and gas-condensate systems during hydrocarbon recovery from natural petroleum reservoirs. Previously a non-equilibrium phase behavior model was proposed as an extension over generally adopted equilibrium models. It is based on relaxation of component chemical potentials difference between phases and provides accurate calculations in some typical situations when non-instantaneous changing of phase fractions and compositions in response to variations of pressure or total composition is to be considered. In this paper we present a thermodynamic analysis of the relaxation model. General equations of non-equilibrium thermodynamics for multiphase flows in porous media are considered, and reduced entropy balance equation for the relaxation process is obtained. Isotropic relaxation process is simulated for a real multicomponent hydrocarbon system with different values of characteristic relaxation time using the non-equilibrium model implemented in the PVT Designer module of the RFD tNavigator simulation software. The results are processed with a special algorithm implemented in Matlab to calculate graphs of the total entropy time derivative and its constituents in the entropy balance equation. It is shown that the constituents have different signs, and the greatest influence on the entropy is associated with the interphase flow of the major component of the mixture and the change of the total system volume in the isotropic process. The characteristic relaxation time affects the rate at which the entropy is approaching its maximum value.

1. Introduction

In terms of chemical composition, oil and natural gas are complex mixtures consisting of a variety of hydrocarbon and non-hydrocarbon components. A hydrocarbon mixture under reservoir conditions can form different phases, in most cases – the liquid phase (oil or condensate) and the gas phase. During the development of petroleum reservoirs, due to changes in external thermobaric parameters and total composition of the mixture, mass transfer occurs between the phases in the hydrocarbon system, which is known as phase transitions. Accurate description of these phenomena makes it possible to justify and optimize technological solutions for hydrocarbon recovery and increase production of petroleum fluids from wells.

Although phase behavior of hydrocarbons is considered mainly within the framework of equilibrium processes [1, 2], in real cases (laboratory or field conditions) non-equilibrium phase behavior is quite often observed. It is related to phase transition hysteresis and is evident for processes...
like condensation of heavier hydrocarbons during cooling of the mixture and their subsequent evaporation during heating [3], or during pressure decrease due to hydrocarbon production and its subsequent increase when wells are stopped or a displacement agent is injected into the reservoir [4].

To account for non-equilibrium phase behavior, a locally equilibrium mathematical model can be considered, but with addition of new parameters that characterize non-equilibrium processes on a larger scale [5]. An important parameter is the characteristic relaxation time which controls the relaxation rate for the fractions and compositions of the phases to their equilibrium values. Practically, the relaxation time determines, for example, the possibility to dissolve released gas back in oil or evaporate liquid condensate to the gas phase. Therefore, it is of fundamental importance for evaluating the effectiveness of secondary and tertiary methods of oil and gas-condensate recovery after the pressure decreases below the saturation point of the initial reservoir fluid.

In this paper we present a thermodynamic analysis of the non-equilibrium phase behavior model [5] based on relaxation of quantities associated with diffusive interphase mass transfer. In this model, relaxation of pressure and temperature is assumed instantaneous, and the interphase exchange is considered separately from the flow of phases.

2. Thermodynamics of processes in porous media

Following classical description of locally-equilibrium processes [6] and adopting derivations presented in [7], the first law of thermodynamics for different parts of a porous medium, in terms of volume-specific entropy balance equation, can be expressed as follows:

\[
dU = T_d dS - p_d dV + \sum_{\alpha \in C} \mu_{\alpha} dN_{\alpha} - d(\phi_{\alpha} u_{\alpha}) = T_d d(\phi_{\alpha} s_{\alpha}) - p_d d\phi_{\alpha} + \sum_{\alpha \in C} \mu_{\alpha} d(\phi_{\alpha} c_{\alpha}) \tag{1}
\]

\[
dU_{(k,l)} = T_{(k,l)} dS_{(k,l)} + \gamma_{(k,l)} dA_{(k,l)} \rightarrow d(a_{(k,l)} u_{(k,l)}) = T_{(k,l)} d(a_{(k,l)} s_{(k,l)}) + \gamma_{(k,l)} dA_{(k,l)} \tag{2}
\]

\[
dU_r = T_r dS_r \rightarrow d(\phi_r u_r) = T_r d(\phi_r s_r) \tag{3}
\]

Here equation (1) is valid for every fluid phase \( \alpha \in P \), (2) – every interface \( \{k, l\} \in I(\varepsilon) \), (3) – rock matrix \( r \); \( U \) is the internal energy, \( T \) is the temperature, \( S \) is the entropy, \( p \) is the pressure, \( V \) is the volume, \( N \) is the amount of substance (number of moles), \( \mu_{\alpha} \) is the chemical potential of component \( i \in \mathcal{C} \) in the fluid phase \( \alpha \), \( \gamma_{(k,l)} \) is the surface tension at the interface \( \{k, l\} \), \( A_{(k,l)} \) is the interface area of \( \{k, l\} \), \( c_{\alpha,i} \) is the molar concentration of component \( i \) in the fluid phase \( \alpha \); \( u \) is the volume-specific internal energy, \( s \) is the volume-specific entropy, \( \alpha \) is the volume-specific interface area, \( \phi_{\alpha} \) and \( \phi_r \) are the volume fractions of fluid phases and rock matrix, respectively.

Component molar balance and total entropy balance equations take the form [7]:

\[
\frac{\partial (\phi_{\alpha} c_{\alpha,i})}{\partial t} + \text{div}((\phi_{\alpha} c_{\alpha,i} u_{\alpha})) = \sum_{\beta \in P} \Lambda_{\alpha,\beta}^{n_{\alpha,i}} \tag{4}
\]

\[
\frac{\partial s}{\partial t} + \text{div}(\varphi s) = \Psi \tag{5}
\]

\[
\Psi = -\frac{1}{2} \sum_{p,p',\varepsilon \in \mathcal{U}(\varepsilon)} (\tau_{p} - \tau_{p'}) A_{p,p'}^{u} - \frac{1}{2} \sum_{\alpha,\beta \in P; \varepsilon \in \mathcal{C}} (v_{\alpha}^{i} - v_{\beta}^{i}) \Lambda_{\alpha,\beta}^{n_{\alpha,i}} - \sum_{p \in \mathcal{P}(\varepsilon) \cup \mathcal{U}(\varepsilon)} \frac{f_{p}^{m}}{p_{a}} \cdot \nabla \tau_{p} - \sum_{\alpha,\beta \in P; \varepsilon \in \mathcal{C}} f_{\alpha}^{n_{\alpha,i}} \cdot \nabla v_{\alpha}^{i} - \sum_{\alpha \in P} \frac{1}{T_{\alpha}} q_{\alpha}(\nabla p_{\alpha} - \rho_{\alpha} g) + \sum_{\alpha \in P} \frac{p_{a}}{T_{\alpha}} \frac{\partial \phi_{\alpha}}{\partial t} - \sum_{\{k,l\} \in \mathcal{I}(\varepsilon)} \gamma_{(k,l)} \frac{\partial a_{(k,l)}}{\partial t} \tag{6}
\]

Here \( \phi_{\alpha}^{n_{\alpha,i}} \) is the molar flux of component \( i \) in the fluid phase \( \alpha \), \( \Lambda_{\alpha,\beta}^{n_{\alpha,i}} \) is the molar rate of component \( i \) received by the fluid phase \( \alpha \) from fluid phase \( \beta \), \( s \) is the total volume-specific entropy,
\( \varphi^5 \) is the total entropy flux, \( \Psi \) is the rate of local entropy production, \( \tau_p = -\frac{1}{T_p} \Lambda_{p,p}^u \) is the volume rate of energy received by the part \( p \) of the porous system from the part \( p' \), \( \nu^i = \mu^i / T \alpha \), \( f^i_p \) is the heat flux through the part \( p \) of the porous system, \( f^{n,i}_a \) is the molar diffusive flux of the component \( i \) in the fluid phase \( \alpha \), \( q_a \) is the mass average velocity and \( \rho_a \) is the mass density of the fluid phase \( \alpha \), \( g \) is the gravitational acceleration.

Equation (5) and expression (6) are considered in more detail later to analyse total entropy changes during the relaxation process.

3. The non-equilibrium phase behavior model

Mathematical models commonly used to simulate phase behavior of hydrocarbon mixtures (oil and gas-condensate) are based on the equilibrium assumption. Typically up to two hydrocarbon phases – liquid and gas/vapor – can coexist, and interaction with rock surface and capillary effects are insufficient. Equilibrium conditions are expressed in terms of equality of chemical potentials between phases for every component of the mixture [1, 2]. Chemical potentials in the liquid and vapor phases are related to fugacities:

\[
\mu^i_L = \text{RTln} f_{i,L} + \mu^i_0, \quad \mu^i_V = \text{RTln} f_{i,V} + \mu^i_0, \quad i = 1..N, \tag{7}
\]

where \( N \) is the number of components in the mixture; \( \mu^i_L \) and \( \mu^i_V \) are the chemical potentials, and \( f_{i,L} \) and \( f_{i,V} \) are the fugacities of the component \( i \) in the liquid and vapor phases at current pressure \( p \) and temperature \( T \); \( R \) is the universal gas constant; \( \mu^i_0 \) is the chemical potential of the component \( i \) in the ideal gas state at the temperature \( T \) and unit pressure.

Taking into account normalization of the liquid and vapor phase fractions and compositions, and assuming that pressure, temperature and component concentrations in the mixture \( z_i \) (mixture composition) are known, the equality conditions are reduced to the following system of equations called the ‘flash’ problem [1, 8]:

\[
\begin{align*}
\ln f_{i,L} - \ln f_{i,V} &= 0, \quad i = 1..N, \\
x_i L + y_i V - z_i &= 0, \quad i = 1..N, \\
\sum_{i=1}^{N} y_i - 1 &= 0, \\
L + V &= 1,
\end{align*}
\tag{8}
\]

where \( L \) and \( V \) are the mole fractions of the liquid and vapor phases, and \( x_i \) and \( y_i \) are the mole concentrations of components in the liquid and vapor phases (phase compositions).

For processes in hydrocarbon systems with non-equilibrium phase behavior, the equality of chemical potentials is no longer valid, and it is necessary to apply a mathematical model of non-equilibrium phase transitions. For practical cases, pressure and temperature relaxation within the fluid system can be assumed instantaneous, while relaxation of the phase fractions and compositions is controlled by diffusive interphase mass transfer. For given change in \( p \), and/or \( T \), and/or \( z_i \) over a timestep \( \Delta t \), the relaxation expression for the chemical potentials difference can be used to formulate the non-equilibrium ‘flash’ problem [5]:

\[
\begin{align*}
\ln f_{i,L} - \ln f_{i,V} &= \tilde{\omega}_{i,L-V}, \quad i = 1..N, \\
x_i L + y_i V - z_i &= 0, \quad i = 1..N, \\
\sum_{i=1}^{N} y_i - 1 &= 0, \\
L + V &= 1,
\end{align*}
\tag{9}
\]

where all the values in the left hand side correspond to the current time layer \( j \) for which the solution is to be obtained, and the expression for \( \tilde{\omega}_{i,L-V} \) corresponds to the solution of the relaxation equation over \( \Delta t \) for the difference of chemical potentials. For an isothermal process with fixed total mixture composition it takes the form:

\[ \]
\[ \bar{\omega}_{i,L-V} = [\ln f_{iL}(\chi^{j-1}, p^j) - \ln f_{iV}(\chi^{j-1}, p^j)] \exp(-\lambda \Delta t), \] (10)

Here \( \lambda \) is the inverse of the characteristic relaxation time, \( \chi^{j-1} \) and \( \chi^{j-1} \) are the compositions of the liquid and vapor phases at the previous time layer, and the pressure \( p^j \) corresponds to the current time layer \( j \). Thermodynamically, \( \bar{\omega}_{i,L-V} \) can be also treated as the normalized intensity of the component \( i \) interphase mass transfer [5].

4. Entropy balance for the relaxation process

As a thermodynamic system tends to the equilibrium state, its total entropy must increase and approach maximum. This means that the time derivative of the total entropy should be positive and decrease towards zero. In order to verify this condition for the model (9)-(10) and analyze contributions of various factors to the change in total entropy, we consider an isothermal relaxation process associated with diffusive interphase mass exchange in a two-phase system (liquid phase \( L \) and vapor phase \( V \)).

The general entropy balance equation (5) is reduced as follows. First, since we examine the interphase exchange process separately from the flow of phases, the divergence of the entropy flux is zeroed: \( dt \nu(p^s) = 0 \). Next, we consider in detail the expression for the local entropy production (6):

- Since all fluxes, except for the interphase diffusive exchange, are absent during isothermal relaxation, the terms with \( f^i_p, f^i_c \) and \( q^i \) are zeroed.
- The difference in inverse temperature values also turns to zero for an isothermal process: \((r_p - r_p') = 0 \).
- We assume that the specific interface area \( d_{L,L} \) does not change, so the last term in (6) is also zeroed. In particular, this assumption includes the case of equal phase pressures (no capillary effects), which is typical for models of phase transitions in hydrocarbon mixtures.

Now we substitute the remaining non-zero terms from (6) to the entropy balance equation (5) and take into account that time derivatives for the relaxation process can be considered total:

\[ \frac{ds}{dt} = -\frac{1}{2} \sum_{\alpha, \beta \in P; i \in C} (\nu^i_{\alpha} - \nu^i_{\beta}) \Lambda^i_{\alpha, \beta} + \sum_{\alpha \in P} \frac{p^i}{T} \frac{d\phi^i}{dt}. \] (11)

Then we use the component balance equation (4) to express \( \Lambda^i_{\alpha, \beta} \) (the molar production of component \( i \) in the fluid phase \( \alpha \)):

\[ \frac{d(\phi^i_{\alpha}c^i_{\alpha})}{dt} = \Lambda^i_{\alpha, \beta} \] (12)

Here we recall that in our process the fluxes are zeroed and only two phases can coexist.

Substituting (12) to (11) and recalling that \( \nu^i_{\alpha} = \frac{\mu^i_{\alpha}}{r_{\alpha}}, \ T_{\alpha} = T_{\beta} = T, \ p_{\alpha} = p_{\beta} = p \), we obtain:

\[ \frac{ds}{dt} = -\frac{1}{2} \sum_{\alpha, \beta \in P; i \in C} \frac{1}{T} (\mu^i_{\alpha} - \mu^i_{\beta}) \frac{d(\phi^i_{\alpha}c^i_{\alpha})}{dt} + \sum_{\alpha \in P} \frac{p}{T} \frac{d\phi^i}{dt}. \] (13)

Now we expand the sums over phases and change to their notation corresponding to the non-equilibrium relaxation model (9):

\[ \frac{ds}{dt} = \sum_{i \in C} \left( -\frac{1}{2} \frac{1}{T} (\mu^i_L - \mu^i_V) \frac{d(\phi^i_Lc^i_L)}{dt} - \frac{1}{2} \frac{1}{T} (\mu^i_L - \mu^i_V) \frac{d(\phi^i_Vc^i_V)}{dt} \right) + \frac{p}{T} \frac{d\phi^i_L}{dt} + \frac{p}{T} \frac{d\phi^i_V}{dt}. \] (14)

Since \( \phi^i_Lc^i_L \) and \( \phi^i_Vc^i_V \) are the numbers of moles of the component \( i \) in the phases per unit volume of the mixture, their time derivatives in the relaxation process sum up to zero, and \( \frac{d(\phi^i_Lc^i_L)}{dt} = -\frac{d(\phi^i_Vc^i_V)}{dt} \). Thus,
The molar concentration of component $i$ per unit volume of the liquid phase $c_i^L$ can be expressed in terms of the component molar fraction in the phase $x_i$ and the liquid phase molar density $N_L$: $c_i^L = x_i N_L$. Also the difference in the component chemical potentials is reduced to the difference in logarithms of the component fugacities: $\mu_i^L - \mu_i^V = RT (\ln f_i^L - \ln f_i^V)$.

Taking the initial total volume of the liquid and gas phases as $V_0$, we have to consider that it changes with time during the isochoric process for a fixed amount of mixture. To split the effects, we will use phase fractions $V_\alpha$ ($\alpha = L, V$) of the current total volume of fluids $V_i$ instead of their fractions $\phi_i$ of the initial total volume $V_0$. Therefore, each volume fraction considered in the entropy balance equation must be multiplied by the correction factor $V' = \frac{V_i}{V_0}$ that takes into account the ratio of the current total fluid volume to the initial one:

$$\frac{ds}{dt} = -\sum_{i \in C} \left( R (\ln f_i^L - \ln f_i^V) \frac{d(V_i V' x_i N_L)}{dt} \right) + \frac{p}{T} \left( \frac{d(V_i V' x_i N_L)}{dt} + \frac{d(V_i V')}{{dt}} \right)$$  \hspace{1cm} (16)

According to the model (9), the difference of the component fugacities' logarithms will decrease exponentially during the relaxation process as given by expression (10). We also take into account that $V_L + V_V = 1$. The final form of the entropy balance equation is:

$$\frac{ds}{dt} = -\sum_{i \in C} \left( \omega_i^L V' \frac{x_i N_L}{V'} \cdot R \right) + \frac{p}{T} \left( \frac{dv'}{dt} \right)$$  \hspace{1cm} (17)

From (17) it can be seen that contributions to the changes in the total entropy are made by transfer of each component between phases and by changes in the total volume of the two-phase system.

5. Test case

As a test case, we consider a model of a real multicomponent hydrocarbon mixture with the following composition (Table 1).

Initially, the mixture is in equilibrium state at pressure $p_0 = 100$ bar and temperature $T = 345$ K. Then pressure instantly changes to $p_1 = 110$ bar, and relaxation of phase fractions and compositions at $p_1$ and $T$ is simulated (Table 2).

| Component (pseudo-component) | Mole concentration | Critical temperature, K | Critical pressure, bar | Molecular weight, kg/kg-mol | Critical volume, m$^3$/kg-mol |
|-----------------------------|--------------------|------------------------|------------------------|-----------------------------|-----------------------------|
| 1  | N2-C1             | 0.38448               | 190.0778               | 45.95011                    | 16.11                        | 0.100084                    |
| 2  | CO2-C2            | 0.06715               | 304.7278               | 63.1546                     | 38.38                        | 0.112048                    |
| 3  | C3-C4             | 0.14194               | 386.3167               | 41.14446                    | 48.71                        | 0.215538                    |
| 4  | C5-C6             | 0.06705               | 484.2889               | 33.33201                    | 76.77                        | 0.324591                    |
| 5  | C7-C8             | 0.08994               | 563.4611               | 28.05201                    | 101.79                       | 0.392792                    |
| 6  | C9-C13            | 0.10958               | 638.6611               | 22.74236                    | 143.21                       | 0.582547                    |
| 7  | C14-C24           | 0.08782               | 733.8833               | 15.6442                     | 245.87                       | 1.055034                    |
| 8  | C25+              | 0.05204               | 889.3611               | 12.97524                    | 509.78                       | 1.85669                     |
Table 2. Thermobaric conditions

| \( p_0 \), bar | \( p_1 \), bar | \( T \), K |
|----------------|----------------|----------|
| 100            | 110            | 345      |

Based on the known composition from Table 1, we can build equilibrium \( p-T \) diagram with the phase envelope and visualize the specified pressure change on it (Figure 1). As one can see, it corresponds to a decrease in gas phase fraction in the two-phase region for an oil-type system (to the left of the critical temperature).

**Figure 1.** \( p-T \) diagram of the multicomponent system and the simulated change in pressure. The blue dot is the initial state \((p_0, T)\), the red arrow is the direction to the state \((p_1, T)\)

6. Calculation results
Simulation of the relaxation process with the model \((9)-(10)\) was performed using the PVT Designer module of the RFD tNavigator software [9] for 4 different values of parameter \( \lambda \) (1/day): \( \lambda = 0.001 \), \( \lambda = 0.01 \), \( \lambda = 0.1 \), \( \lambda = 1 \). The results were processed in Matlab.

Figure 2 shows the change in the fractions of light and heavy components in the liquid and vapor phases. When the pressure is increased in a two-phase oil-type system, the gas phase fraction is decreased. Light hydrocarbon components partially move from the gas phase to the liquid phase, and their concentration in the liquid phase is increased. Accordingly, the concentration of heavy hydrocarbon components is decreased. As can be seen from the graphs in Figure 2, the lower the value of \( \lambda \), the faster the component fractions relax to their equilibrium values.

Figure 3 considers the change in the molar densities of the phases. As the pressure is increased, the volume of each phase is decreased due to compressibility. Accordingly, the number of moles per unit volume is increased. But in addition to the changes in volume, another process is imposed. The phases exchange components, which can lead to non-monotonic changes in the molar density, as can be seen in Figure 3 for the gas phase. The closer the system is to the equilibrium state, the less the changes in the component composition of the phases. As the system approaches the equilibrium state, the molar densities reach constant values.

Now let's analyze the entropy behavior during the relaxation process. The time derivative of the volume-specific total entropy was calculated using equation \((17)\).

Figure 4 shows graphs for the time derivatives of the total entropy and its components vs. time for \( \lambda = 0.001 \) 1/day (characteristic relaxation time is 1000 days).
Figure 2. Change in the components’ fractions in the liquid phase $x_i$ and the vapor phase $y_i$ vs. time for different values of $\lambda$.

Figure 3. Change in the molar densities of phases $N_L$ and $N_V$ vs. time for different values of $\lambda$. 
Figure 4. Time derivative of the volume-specific total entropy $\frac{ds}{dt}$ and its components for $\lambda = 0.001$ 1/day

It can be seen from Figure 4 that the greatest effect on the entropy have the change in the fraction of the lightest pseudo-component N2-C1 (with the highest concentration in the mixture) and the change in the total volume of the phases. As expected thermodynamically, the total entropy derivative is positive and relaxes towards the equilibrium null value. Note that this is not true for its constituents: they have different signs and hence different effect on the final behavior of the total entropy. Also, some of them distinctly tend to nonzero values. However, they compensate each other, so that the total entropy derivative tends to zero. But for this value of $\lambda$ relaxation is very slow and simulation time is not enough to achieve the equilibrium state.

Same graphs are shown in Figure 5 for $\lambda = 0.01$ 1/day, i.e., for the characteristic relaxation time of 100 days. A similar situation is observed, but since the characteristic relaxation time is smaller, the entropy reaches its maximum faster, and the graph of the total entropy derivative clearly approaches zero at the end of the simulation time.

Figures 6 and 7 show similar graphs for the two larger values of $\lambda$. In these cases, a good approximation to equilibrium is achieved in a time much less than the total simulation time.

Figure 8 shows a summary graph of the total entropy derivative vs. time for all the considered values of $\lambda$. The higher the value of $\lambda$ (the smaller the characteristic relaxation time), the greater the initial value of the derivative, and the faster entropy tends to maximum (and its derivative – to zero).
Figure 5. Time derivative of the volume-specific total entropy $ds/dt$ and its components for $\lambda = 0.01$ l/day

Figure 6. Time derivative of the volume-specific total entropy $ds/dt$ and its components for $\lambda = 0.1$ l/day
Figure 7. Time derivative of the volume-specific total entropy $\frac{ds}{dt}$ and its components for $\lambda = 1$ 1/day

Figure 8. Graphs of the time derivative of the volume-specific total entropy $\frac{ds}{dt}$ for different values of $\lambda$
7. Conclusions

In this paper we presented entropy-based thermodynamical analysis of the non-equilibrium relaxational phase behavior model for hydrocarbon mixtures [5].

The reduced entropy balance equation was obtained for isothermal relaxation of phase fractions and compositions in a two-phase hydrocarbon system. The equation includes the terms associated with diffusive interphase exchange of components and the change in total volume of the two-phase system.

As an illustrative test case, an isothermal relaxation process was simulated using the model [5] for a real multicomponent oil-type hydrocarbon system. Graphs of component molar fractions in phases, molar densities of the phases, and time derivative of the total entropy and its constituents were calculated and analyzed.

As expected, the total entropy derivative is positive and tends to the equilibrium null value. However, its constituents have different signs and different effect on the final behavior of the total entropy. Some of them distinctly tend to nonzero values but compensate each other, so that the total entropy derivative tends to zero. The greatest influence on the entropy have the interphase exchange for the component with the highest concentration in the mixture and the change in the total volume of the two-phase system.

The key control parameter of the non-equilibrium model is the characteristic relaxation time. The smaller its value, the greater the initial value of the entropy time derivative and the faster the total entropy reaches maximum.

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