Numerical Simulation of Non-Equilibrium Isochoric Phase Transitions in Hydrocarbon Mixtures

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Abstract. Numerical simulations of phase behavior in multicomponent hydrocarbon mixtures is an essential part of petroleum reservoir engineering practice. Almost all industry-adopted models are based on equilibrium assumptions. The condition of Gibbs energy minimum, or equality of chemical potentials, combined with the equation of state (EoS), e.g. the Peng-Robinson EoS, for each phase and with balance conditions for concentrations are used to compute phase mole fractions and compositions (component concentrations in the phases). However, experimental and field data show that in a number of important real situations equilibrium assumptions are not valid. In the previous study of Indrupskiy et al. (Computational Geosciences, 21(5), 2017) a unified model and numerical algorithms were presented for isothermal non-equilibrium phase behavior simulations in petroleum engineering applications. The model is based on the relaxation equation for the component chemical potentials difference between phases. It was verified on field data; however, only integral behavior of the system (a gas-condensate reservoir) was available to be matched. In the current study, we extended the non-equilibrium model to isochoric processes and developed a numerical algorithm which allowed to perform direct simulation of laboratory experiments with a multicomponent hydrocarbon mixture and validate the non-equilibrium model. The experimental data were successfully matched with the model simulations. The model and algorithm are suitable for equilibrium and non-equilibrium isochoric phase behavior simulations with synthetic and real multicomponent hydrocarbon mixtures (oils and gas-condensates).

1. Introduction
In terms of chemical composition, oil and natural gas are complex mixtures, consisting of a variety of hydrocarbon and non-hydrocarbon components. Hydrocarbon mixture under reservoir conditions can form different phases, in most cases – the liquid phase (oil or condensate) and the gas phase. The phase state of the mixture depends on the component composition of the mixture and external thermobaric parameters, and it is permanently changing because of the changes in reservoir pressure and mixture composition during oil or gas production. Hence, there is a need to study phase transitions in hydrocarbon mixtures and changes in their properties depending on pressure and temperature.

Thus, study and prediction of phase behavior and properties of hydrocarbons in oil-, gas- and gas-condensate reservoirs are necessary for justification and optimization of hydrocarbon reservoir development and increase of oil, gas and condensate production. In most cases, calculation of phase
transitions is based on the concept of equilibrium phase behavior [1,2]. However, processes with essentially non-equilibrium phase behavior of hydrocarbons are often observed in laboratory and field conditions [3-5]. In such cases, mathematical model of non-equilibrium phase transitions is to be considered instead of the equilibrium phase behavior model.

In the processes with non-equilibrium phase behavior the hysteresis of phase transitions occurs. The main reason for this is a considerable difference between the transition from the single-phase state to the two-phase state (for example, condensation process in a gas-condensate mixture) and the reverse transition from the two-phase state to the single-phase state (reverse evaporation of condensate). A similar phenomenon is observed for the processes of gas liberation from oil and reverse dissolution at oil deposits [6].

The transition from the single-phase state to the two-phase state is accompanied by formation of a new phase in the bulk of the existing phase and is equilibrium. In the transition of the mixture from the two-phase to the single-phase state, if no forced mixing is performed, the diffusion of components through the interphase boundary is observed. Since the area of interphase contact which controls the components’ mass transfer between phases is limited, it takes a substantial time to establish the equilibrium between the phases, and the non-equilibrium phase behavior is observed. This is the main reason of the phase transition hysteresis [6].

Several authors presented models and algorithms for hydrocarbon flow simulations considering non-equilibrium phase transitions [7-16]. These studies are either aimed at specific purposes like upscaling of the flow model, or propose to introduce incomplete mixing of phases instead of non-equilibrium phase behavior, or require a set of reservoir and fluid parameters that are practically too difficult to be determined.

A unified thermodynamically-consistent model for non-equilibrium phase behavior simulations was proposed in [6]. The model is suitable both for hydrocarbon flow simulations [17] or stand-alone phase behavior simulations (PVT-simulations) [6,18] and is an extension over the equilibrium phase behavior models based on equation-of-state (EoS) calculations [1,2]. In the non-equilibrium case, relaxation of the chemical potentials difference between phases is considered for each component instead of equality of the chemical potentials in the equilibrium case. The control parameter of the model is the inverse characteristic relaxation time which can be determined from laboratory or field data. Verification of the model was performed on field data [6,19], but only integral behavior of the system (a gas-condensate reservoir) was available to be matched. That is, verification of the model on more detailed laboratory data is still required.

In this paper we use the data of isochoric laboratory experiments on non-equilibrium phase behavior of hydrocarbon mixtures for the model verification. As all the previous applications of the model required only isothermal phase behavior calculations, a modified model and a numerical algorithm are developed for calculating isochoric non-equilibrium processes. Using the algorithm, we simulate the experiments and present direct comparison of calculated and lab data to verify the model.

2. Isochoric experiments on non-equilibrium phase behavior of hydrocarbon mixtures

Non-equilibrium phase behavior of hydrocarbon mixtures was studied in a series of isochoric experiments performed by the Phase Transitions and Critical Phenomena lab of the Oil and Gas Research Institute of the Russian Academy of Sciences (OGRI RAS) [20]. During the experiments, a multicomponent hydrocarbon mixture with a given composition (mole fractions of components) \( z_i \), mass density \( \rho \) and initial temperature \( T_{\text{start}} \) was placed in a fixed-volume experimental cell of an adiabatic calorimeter. Initially the mixture was in the single-phase state. Then the cell was progressively cooled down with a specified rate, the isochoric \( p-T \) (temperature-pressure) dependence was measured, and the temperature of the equilibrium phase transition \( T_{\text{trans}} \) for the isochore was determined. Further cooling of the system was characterized by equilibrium phase behavior, with increasing second (vapor) phase fraction. The lowest temperature reached at cooling \( T_{\text{min}} \) (being the starting temperature for the further heating) was determined approximately by the condition
\( \frac{T_{\text{trans}} - T_{\text{min}}}{T_{\text{min}}} \approx 0.2 \). Starting from \( T_{\text{min}} \), reverse heating of the system was performed with the same rate as the previous cooling. The heating process was characterized by non-equilibrium phase behavior of the mixture with pronounced hysteresis, and the temperature of mixture transition from the two-phase state to the single-phase state differed significantly from the equilibrium phase transition temperature. The hysteresis 'amplitude' was found to depend on the 'depth' of cooling (\( T_{\text{min}} \)), as well as on the duration of pause between cooling and heating.

If the heating process was paused at the equilibrium phase transition temperature, pressure relaxation was observed corresponding to the relaxation of the system to the equilibrium state. When the heating was continued after relaxation, the \( p-T \) curve repeated the equilibrium one observed during cooling.

Fig. 1 shows the \( p-T \) diagram obtained during one of experiments with a three component-mixture of 50% (mole percent) methane, 35% propane and 15% pentane. The process of cooling the system, which is characterized by equilibrium phase behavior, corresponds to the blue curve (isochore) on the graph. One can see the sharp bend on the isochore at the temperature of 340K which corresponds to the phase transition from the single-phase liquid state to the two-phase state, when the gas liberation from the liquid phase began. The initial temperature in the experiment was 365K, and cooling was carried out down to the temperature of 300K. The reverse heating of the system, which was characterized by non-equilibrium phase behavior, is presented by the orange isochore in Fig. 1. In this case, hysteresis of the phase transition is clearly observed. At the equilibrium phase transition temperature of 340.6K, the heating was stopped, and the following pressure relaxation is displayed by the vertical segment (red line) in Fig. 1. This process is also shown in Fig. 2 as a pressure dependence on time during relaxation. After the establishment of equilibrium, the system was continued to heat up. In this case, it demonstrated the equilibrium phase behavior, which corresponds to the upward movement along the inclined red line in Fig. 1.

Thus, from the results of the experiment, the hysteretic \( p-T \) dependence (Fig. 1), the value of the characteristic relaxation time estimated from the pressure relaxation curve (Fig. 2) and the rate of cooling / heating \( \frac{\Delta T}{\Delta t} \) were determined. Here \( \Delta T \) is the temperature change over the time period of \( \Delta t \).

![Figure 1](image_url)

**Figure 1.** The \( p-T \) diagram for the considered experiment [20]
Figure 2. Graph of the pressure relaxation at the equilibrium phase transition temperature [20]

3. The non-equilibrium phase behavior model

Mathematical models commonly used to simulate phase behavior of hydrocarbon (oil and gas-condensate) mixtures are based on the equilibrium assumption, which is expressed in terms of the equality of chemical potentials between phases for every component of the mixture [1,2].

The chemical potentials of the component \(i\) in the liquid and vapor phases can be expressed as

\[
\mu_{i,L} = RT \ln f_{i,L} + \mu_i^0, \quad \mu_{i,V} = RT \ln f_{i,V} + \mu_i^0, \quad i = 1..N,
\]

(1)

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, one arrives at the so-called 'flash' problem for the equilibrium case given by the following system of equations [2]:

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

(2)

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).

Using equation of state (EoS) for the liquid and vapor phases, i.e. the Peng-Robinson EoS [1], the fugacities are expressed by the known functions of pressure, temperature and phase compositions. Then the system (2) turns into a set of nonlinear algebraic equations for the basic variables \(L, V, x_i\) and \(y_i\), and several well-developed methods can be used to find the solution [1,2].

In the equilibrium case, the dynamic processes with changing pressure, temperature and mixture composition can be simulated by repeated solution of the system (2) for sequential values of \(p\), and/or \(T\), and/or \(z_i\).

To simulate processes with non-equilibrium phase behavior, it is necessary to apply a mathematical model of non-equilibrium phase transitions [6]. In this case, the equality of chemical potentials is no
longer valid. However, one can treat the dynamic process as a step-wise in time. Assuming the nested two-stage procedure with the given change in \( p \), and/or \( T \), and/or \( z_i \) over the current timestep \( \Delta t \) as the outer stage, and the relaxation of the phase fractions and compositions during \( \Delta t \) as the inner stage, one can arrive at the non-equilibrium flash system [6]:

\[
\begin{aligned}
\ln f_{iL} - \ln f_{iV} &= \bar{\omega}_{iL-V}, & i &= 1..N, \\
x_iL + y_iV - z_i &= 0, & i &= 1..N, \\
\sum_{i=1}^{N} y_i - 1 &= 0, \\
L + V &= 1,
\end{aligned}
\] (3)

where all the values in the left hand side correspond to the current time layer \( j \) for which the solution is to be obtained.

The expression for \( \bar{\omega}_{iL-V} \) is derived from the solution of the relaxation equation for the difference of chemical potentials over the timestep. For an isochoric process with fixed mixture composition, it takes the following form:

\[
\bar{\omega}_{iL-V} = [\ln f_{iL}(\bar{x}^{j-1}, p^j) - \ln f_{iV}(\bar{y}^{j-1}, p^j)]\exp(-\lambda \Delta t). \] (4)

Here \( \lambda \) is the inverse of the characteristic relaxation time, \( \bar{x}^{j-1} \) and \( \bar{y}^{j-1} \) are the compositions of the liquid and vapor phases at the previous time layer, and the pressure \( p^j \) refers to the current time layer \( j \).

Thermodynamically, \( \bar{\omega}_{iL-V} \) can be also treated as the normalized intensity of the component interphase mass transfer [18].

Since the systems (2) and (3) differ only by the right-hand sides, the solution procedure in the non-equilibrium case is only slightly different from the one in the equilibrium case [6].

4. Simulation of equilibrium and non-equilibrium isochoric phase transitions

Both the equilibrium (2) and non-equilibrium (3) flash problem formulations are suitable for the processes with independent changes of pressure and temperature, including the isothermal processes particularly important for petroleum reservoir applications.

Lab experiments in fixed-volume cells correspond to isochoric processes. This means that cooling or heating of the system results not only in temperature changes, but also in dependent changes in pressure. Thus, pressure becomes one of the unknowns to be determined by the solution of the flash problem. Also, the isochoric condition has to be considered.

Combining the systems (2) and (3) in a unified formulation and taking into account preservation of the total density (equivalent to preservation of the total volume) of the mixture, we obtain the following flash problem formulation for the isochoric processes:

\[
\begin{aligned}
\ln f_{iL} - \ln f_{iV} &= \bar{\omega}_{iL-V}, & i &= 1..N, \\
x_iL + y_iV - z_i &= 0, & i &= 1..N, \\
\sum_{i=1}^{N} y_i - 1 &= 0, \\
L + V &= 1,
\end{aligned}
\] (5)

where \( \rho_L \) and \( \rho_V \) are the molar densities of the liquid and vapor phases, respectively; \( u \) is the volume fraction of the liquid phase, and \( (1 - u) \) – of the vapor phase; \( \rho_0 \) is the total molar density of the mixture.

Thus, simulation of isochoric processes with phase transitions is based on the consequent solution of the system (5) for phase fractions, compositions and pressure at each simulation time step corresponding to the known change in temperature. EoS-based expressions for fugacities and molar densities substituted to the equations (5) provide the resulting set of nonlinear algebraic equations which are solved by the Newton’s method.
In the single-phase state of the mixture, the system (5) is reduced to the only last equation for density with \( u = 0 \) or \( u = 1 \). Then the method of successive substitutions is used to find the value of pressure for the current value of temperature.

For equilibrium phase transitions, \( \tilde{\omega}_{iL\tau} = 0 \).

In the non-equilibrium case, a certain correction has to be introduced to the expression (4) for the intensities of the interphase mass transfer. To derive the expression for \( \tilde{\omega}_{iL\tau} \), we use the same approach as in the isothermal case [6], but with the temperature being the changing external parameter. In addition, in contrast to the formula (4), one has to take into account that any change in the temperature in the isochoric case results in the change in pressure, so that the total mixture density is preserved. The resulting expression is:

\[
\tilde{\omega}_{iL\tau} = \left[ \ln f_{iL}(\tilde{x}^{j-1}, \tilde{p}^{j-1}, T^j) - \ln f_{iV}(\tilde{y}^{j-1}, \tilde{p}^{j-1}, T^j) \right] \exp(-\lambda \Delta t).
\]  

(6)

Here \( \tilde{p}^{j-1} \) is the 'intermediate' value of pressure, which corresponds to preservation of the total mixture density \( \rho_0 \) at the new value of temperature \( T^j \), but with the previous phase fractions \( L^{j-1} \), \( V^{j-1} \) and phase compositions \( \tilde{x}^{j-1}, \tilde{y}^{j-1} \). It is found by solving the last equation of the system (5) for pressure by successive substitution, similar to the single-phase case.

Formula (6) is explained as follows. Each step of the non-equilibrium isochoric process we virtually divide into two stages.

In the first stage, only the change in the 'external' parameters is considered, with no mass transfer between phases. This means that the temperature changes from \( T^{j-1} \) to \( T^j \) at fixed \( L^{j-1}, V^{j-1}, \tilde{x}^{j-1} \), and \( \tilde{y}^{j-1} \). However, since the total mixture density has to be preserved, the pressure also changes from \( p^{j-1} \) to some 'intermediate' value \( \tilde{p}^{j-1} \), such that the isochoric condition is satisfied at \( T^j, L^{j-1}, V^{j-1}, \tilde{x}^{j-1}, \tilde{y}^{j-1} \), and \( \tilde{p}^{j-1} \).

In the second stage, we consider the interphase mass transfer (component diffusion) that occurs as the response to the change in temperature and pressure. It can be expressed in terms of relaxation of the normalized differences in chemical potentials of components between phases during the timestep \( \Delta t \). For any mixture component \( i \), this difference after the first stage is \( \ln f_{iL}(\tilde{x}^{j-1}, \tilde{p}^{j-1}, T^j) - \ln f_{iV}(\tilde{y}^{j-1}, \tilde{p}^{j-1}, T^j) \), which is the first factor in the expression (6). Solution of the relaxation equation over the timestep \( \Delta t \), with the given inverse characteristic relaxation time \( \lambda \), results in the second factor in (6). Thus, the right hand side of (6) equals to the normalized difference in chemical potentials for the component \( i \) between phases at the end of the timestep. And it is the same value as in the left hand side of the first equation (5), which finally explains the formula (6).

Note that during the relaxation over the timestep mole fractions of phases are changing from \( L^{j-1} \) and \( V^{j-1} \) to \( L^j \) and \( V^j \), and phase compositions – from \( \tilde{x}^{j-1} \) and \( \tilde{y}^{j-1} \) to \( \tilde{x}^j \) and \( \tilde{y}^j \). At the same time, due to the isochoric condition, pressure is changing from \( \tilde{p}^{j-1} \) to \( p^j \), so that the total mixture density is preserved. These features are intrinsically taken into account in the left hand side of equations (5) and by inclusion of \( p^j \) in the set of the basic variables.

Also note that if at some non-equilibrium state the temperature is fixed, solution of (5) for successive timesteps provides the pressure relaxation dynamics as the response to the relaxation of the system towards the equilibrium state at this temperature.

Solution of the system (5) corresponds to the current non-equilibrium state of the system, and its deviation from the equilibrium state depends on \( \lambda \) and the rate of temperature change \( \frac{\Delta T}{\Delta t} \). Obviously, when \( \lambda \to \infty \), the system tends to the equilibrium phase behavior.

As a graphical interpretation, Fig. 3 shows hypothetical graphs of the reduced Gibbs energy for two values of temperature versus one of the free parameters – e.g., mole fraction of a certain mixture component in one of the phases. The equilibrium state of the system at the temperature \( T_1 \) corresponds to the minimum Gibbs energy \( \tilde{g}^*_m \), and at the temperature \( T_2 \) to \( \tilde{g}^*_{m\ min} \). In the equilibrium case, as the temperature changes from \( T_1 \) to \( T_2 \), the system instantly jumps from the state with \( \tilde{g}^*_m \) on the solid line to the state with \( \tilde{g}^*_m \) on the dashed line.
In the non-equilibrium case, the first stage is the change in temperature, which results in the change of the Gibbs energy curve from the solid one to the dashed one with no change to the free parameters (phase fractions and compositions). This is shown in Fig 3 by vertical arrow lines for two situations: either when at \( T_1 \) the system was in the equilibrium state \( g_{\text{min}}^* \) or in some non-equilibrium state \( g^* \). Although the free parameters are not changed at the first stage, the isochoric condition implies that the vertical arrow lines also correspond to changes in pressure to some intermediate values.

The second stage is the relaxation of the system at fixed temperature \( T_2 \), which is the process of changing the free parameters (phase fractions and compositions) towards the equilibrium state – the Gibbs energy minimum \( g_{\text{min}}^* \) (thick black arrow line in Fig. 3). Note that pressure is also changing during this process due to the isochoric condition. The final position of the system state on the dashed curve depends on \( \lambda \) and \( \Delta t \).

**Figure 3.** Hypothetic graphs of reduced Gibbs energy at \( T_1 \) (solid line) and \( T_2 \) (dashed line)

The overall simulation algorithm for the non-equilibrium isochoric processes consists of two nested loops (Fig. 4). The external loop corresponds to the change in temperature over time, and at each timestep the intensities of the components' interphase mass transfer are recalculated. In the inner loop, the system of equations (5) is solved by the Newton's method, and the values for the base variables are adjusted. After adjusting the values of the base variables, the algorithm proceeds to the next timestep, and the process is repeated for the new temperature.

The simulation algorithm was implemented as a numerical code in C++ suitable for equilibrium and non-equilibrium phase behavior calculations for general hydrocarbon mixtures under isochoric processes.

5. Simulation of the lab experiments

Using the numerical code, the laboratory experiment described in the Section 2 (Fig. 1 and Fig. 2) was simulated. The three-component hydrocarbon mixture of 50% methane, 35% propane and 15% pentane (C1+0.35C3+0.15C5) is considered in the experiment with the mass density \( \rho_0 = 290 \text{ kg/m}^3 \). Heating and cooling are carried out in the temperature range of 300K to 365K with a cooling/heating rate of 2K per hour (Fig. 1). The experimental pressure relaxation curve (Fig. 2) derived the characteristic relaxation time \( t_{\text{relax}} = 14700 \text{ s} \).
Fig. 4. Flowchart of the simulation algorithm

Fig. 5 presents a comparison of the experimental and simulated p-T diagrams. The solid lines correspond to the simulated data, while the circle marks designate experimental data. The blue curve describes the equilibrium cooling process, while the red one stands for the non-equilibrium heating.

A generally good agreement of the simulation results with the experimental data was achieved. Vertical deviation of the non-equilibrium curve from the equilibrium one is practically the same for the experimental and simulated curves, that is, the model correctly reproduces the phase transition hysteresis. Some deviations of the calculated curve from the experimental one are observed both on the equilibrium and non-equilibrium branches of the graph. This indicates that they’re related not to the quality of the non-equilibrium model, but to the limited accuracy of density calculations by the Peng-Robinson EoS, even using shift parameters [1]. This is also the reason why the simulated non-equilibrium curve shows a slightly earlier transition from the two-phase state to the single-phase state. But general behavior of the non-equilibrium branch is correctly reproduced without any adjustment of the characteristic relaxation time (λ was set to 1/14700 s⁻¹), which indicates the adequacy of the mathematical model.

Fig. 6 shows that the characteristic relaxation time $t_{relax} = 1/\lambda$ significantly affects the amplitude of the phase transition hysteresis. The graphs correspond to the simulated p-T diagrams for different values of $t_{relax}$. In Fig. 5, consistency of experimental and calculated data is achieved for the correct experimental value of $t_{relax} = 14700$ s (curve 2 in Fig. 6). The greater the value of $\lambda$ (i.e., the less the value of $t_{relax}$), the closer the simulated non-equilibrium curve to the equilibrium one, which means that relaxation is faster than in the experiment (curve 3, Fig. 6). On the contrary, for smaller values of $\lambda$ (greater values of $t_{relax}$) the hysteresis is higher, that is, the relaxation is slower than in the experiment (curve 4, Fig. 6). Recall that the 'amplitude' of the hysteresis depends not solely on $t_{relax}$, but on its combination with the rate of temperature changes.
Figure 5. Experimental (circle marks) and simulated (solid lines) $p$-$T$ diagrams

Figure 6. Simulated $p$-$T$ diagrams for different values of $t_{\text{relax}} = 1/\lambda$:
1 – equilibrium; 2 – 14700 s; 3 – 7000 s; 4 – 50000 s
In Fig. 7 we present a comparison of the simulated and experimental graphs of pressure versus time for the isochoric relaxation of the system to the equilibrium state at the temperature of equilibrium phase transition $T_{\text{trans}}$. In Fig. 5, this process was shown by the vertical segment of the red line at the $T_{\text{trans}}=340.6\,\text{K}$. The calculated and measured curves demonstrate a similar behavior, but do not coincide exactly, since the experimental graph does not strictly follow the exponential dependence typical for relaxation. This may be attributed to the difference in relaxation times in the diffusion processes for different components of the mixture and require further investigation.

To show the specifics of relaxation for different mixture parameters, we also present the simulated time dependences of the vapor phase molar fraction $V(t)$ (Fig. 8) and molar fractions of components in the liquid phase $x_i(t)$ (Fig. 9-11) at the temperature $T_{\text{trans}}=340.6\,\text{K}$. Note that relaxation is mainly characterized by the methane dissolution in the liquid phase with decreasing $V$, $x_2$ and $x_3$, and increasing $x_1$. Also note that equilibrium asymptotes for $x_i$ equal to $z_i$, which is correct for the transition to the single-phase state.

Figure 7. Simulated (blue) and experimental (brown) pressure relaxation curves at $T_{\text{trans}}=340.6\,\text{K}$

Figure 8. Simulated graph of the vapor phase molar fraction versus time during relaxation at $T_{\text{trans}}=340.6\,\text{K}$
Figure 9. Simulated graph of the methane molar fraction in the liquid phase versus time during relaxation at $T_{\text{trans}}=340.6\text{K}$

Figure 10. Simulated graph of the propane molar fraction in the liquid phase versus time during relaxation at $T_{\text{trans}}=340.6\text{K}$
Figure 11. Simulated graph of the pentane molar fraction in the liquid phase versus time during relaxation at $T_{\text{trans}}=340.6\text{K}$

If the system is continued to heat after the equilibrium at $T_{\text{trans}}$ is established, the change in pressure is characterized by equilibrium behavior and corresponds to the upward movement along the lower (blue) curve shown in Fig. 5.

6. Conclusions
In this paper, we addressed the simulation of non-equilibrium phase behavior of hydrocarbon mixtures for isochoric processes which are typical for laboratory studies in fixed-volume cells.

- A modification to the previously proposed mathematical model for non-equilibrium phase transitions in hydrocarbon mixtures [6] was presented which allows to simulate isochoric processes.
- A numerical simulation algorithm for isochoric processes with equilibrium and non-equilibrium phase transitions was developed and implemented in a general software code in C++.
- Numerical simulations of isochoric laboratory experiments with three-component hydrocarbon mixtures were performed. The results made it possible to verify the mathematical model of non-equilibrium phase transitions in multicomponent hydrocarbon fluids using experimental data.

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