Prediction of thermodynamic properties of natural gases using Monte Carlo simulations

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Abstract. In this paper an applications of Monte-Carlo simulation in natural gas production is presented. We have investigated model of natural gas of the Bavlinskoye deposit located in the southeast of the Republic of Tatarstan. For this natural gas and for pure methane and ethane gases we have obtained thermal expansivity, isothermal compressibility, compressibility factor, heat capacity, Joule-Thompson coefficient and density at pressures up to 110 MPa at deposit temperature (463 K). Also we have obtained vapor pressures and liquid-vapor phase diagrams. Simulated properties for methane are in a good agreement with available experimental data.

1. Introduction

Today there are a number of problems in oil and gas industry related to the correct description of heavy hydrocarbons properties. Furthermore problems are encountered toxic and corrosive materials, unstable systems, microporous adsorbents, systems at extreme pressures. Natural gases are mixtures in which gaseous hydrocarbons (mainly methane) are most abundant, but they can contain significant amounts of liquid hydrocarbons, which affect strongly on the thermodynamic properties.

The properties of natural gases as well as other mixtures often can not be obtained from the superposition of their component properties that is why we should consider this system as complex.

Molecular simulation methods allow to predict all thermodynamic properties at all conditions and in the absence of phenomenological parameters. Molecular simulation is an emerging technique, which consists in performing a detailed simulation of microscopic systems involving typically a few hundreds or even thousands of molecules. On the basis of these simulations, appropriate statistical averages are performed to obtain the quantities that can be compared with experimental measurements.

2. Monte Carlo method

Molecular simulation includes methods of quantum chemistry and statistical thermodynamics. The important point is a choice of a statistical ensemble most suitable for the desired application [1]. In brief, the chosen statistical ensemble considers the possible states of a system compatible with some set of constraints, such as imposed temperature or imposed number of molecules. Practically, there are two main methods to simulate statistical ensembles. The first is molecular dynamics, which consists in solving the equations of motion, and the second is Monte Carlo (MC) simulation, in which a statistical method is used. According to the ergodic hypothesis they should give equal average values.

In the present work we used the method of Monte Carlo. The main point of this method is random transitions between states of the system with a probability determined by the given statistical ensemble. At each MC step randomly selected particle (or group of particles) is moved randomly. This

causes the potential energy changes by a certain amount. Then the energy difference determines the transition probability from the "old" to the "new" state of the system. System parameters are calculated and are averaged over large number of steps. The potential energy of the molecular system consists of Lennard-Jones interaction and electrostatic interaction and intramolecular interactions associated with the stretching, bending and torsion of the molecules:

$$U = \sum_{i,j} U_{i,j}^{LJ} + \sum_{i,j} U_{i,j}^{el} + \sum_{k} U^{stretch}(l_k) + \sum_{m} U^{bend}(\theta_m) + \sum_{n} U^{tors}(\varphi_n) \,. \qquad (1)$$

The Monte Carlo simulations have wide range applications in different field of oil and gas industry.

- Method could be used to determine the unknown physical parameters of heavy hydrocarbons. In the case of the lack of experimental data for hydrocarbons, Monte Carlo simulations can be performed in order to obtain useful information for petroleum engineers such as saturation pressures, vaporization enthalpies and liquid densities at different temperatures.

- The method allows to determine thermophysical properties of natural gases. Molecular simulation can be used to predict the behaviour of such systems at all conditions, including very high pressures. It is also possible to determine the compressibility factor ($Z = PV / RT$), specific heat capacities, thermal expansion and isothermal compressibility with rather high accuracy.

- It should be noted, that in some natural deposits the pressure can reach 110 MPa and temperatures of 460 K or higher. Under these conditions, the natural gas can heat during the production process . The sign of the Joule-Thomson (JT) coefficient explains this feature and this fact should be considered during construction of wells. However, it is rather problematically to measure the Joule-Thomson coefficient in representative conditions due to experimental difficulties as well as small amount of gas sample available (a few hundreds of cm^3). Some estimations for JT coefficient from the equations of state are possible but usually with a large error, because these equations have not been validated for the extreme conditions, so that molecular simulation is a good candidate method.

- Furthermore molecular simulation is efficient tool to predict phase diagrams and phase densities, to determine solubility of gases, for example, in polymer coatings of pipes, it is also very useful to understand and predict the adsorption properties of zeolites, which are often used for separations in hydrocarbon processing.

3. Calculations

In this section we present calculations for the natural gas of the Bavlinskoye deposit located in the south-east of the Republic of Tatarstan. Similar calculations can be performed for any other natural gas. In addition, we also carried out calculations for methane and ethane in order to compare our results for these gases with known experimental data.

The calculations were performed by means of GIBBS code embedded in MedeA© interface. The periodic boundary conditions for simulation box were implied. We used Lennard-Jones (6-12) nonbond potentials [2-5] with the Lorentz-Berthelot mixing rule. The cutoff radius was one-half of the box length. The charges are being ignored, because the number of molecules described with electrostatic charges (CO_2) is rather small, and their electrostatic interaction energy is negligible. For a heavy alkanes the bending potential and the torsion potential were used as well. For more details about the Monte Carlo method as well as the calculation of interaction energy see, for example, Ref. [6]. In order to obtain the converging results, up to $3*10^7$ MC steps were used, whereas for the calculation of average values only last 50% of data were taken.

3.1. Densities

Percentage of components constituting the natural gas from the Bavlinskoye deposit is presented in Table 1. Firstly, we calculated the density of each component in the mixture at normal conditions in order to compare with known experimental data. The results are presented in the Figure 1. Computational error does not exceed $\approx 6.5\%$.

In the Figure 2 we can see density of methane and natural gas in a range of pressure from 30 to 110 MPa at a temperature of 463 K. The figure also shows that the experimental data from [7] for methane are in a good agreement with our calculations.

Table 1. Percentage of components constituting the natural gas from the Bavlinskoye deposit.

| Component	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}	N_2	CO_2
Percentage	35	20.7	19.9	9.8	5.8	8.4	0.4
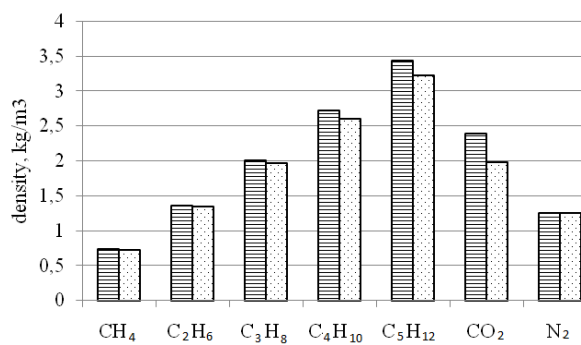
Figure 1. Density of each component of natural gas from the Bavlinskoye deposit at normal conditions ($\equiv$ - simulation, $\therefore$ - experimental data [7]).
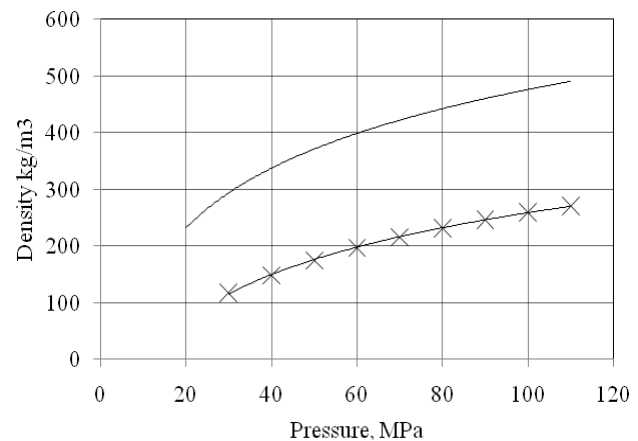
Figure 2. The calculated reassure dependence for the density of gases at T=463 K: the upper curve - natural gas of the Bavlinskoye deposit; the bottom curve - the methane ($\times$ - the experimental data [7]).

3.2. The Joule-Thompson coefficient and inversion pressure

Simulation results for Joule-Thomson coefficient are shown in Figure 3, where the computed Joule-Thomson coefficient of the natural gas from the Bavlinskoye deposit is plotted versus pressure at deposit temperature (463 K). We also present simulation results for methane and ethane. Those results could be partly confirmed by a measurement of the inversion pressure, *i.e.* the pressure corresponding to the change of sign of the Joule-Thomson coefficient (it can be obtained from volumetric measurements). Inversion pressures are collected in Table 2. For comparison, we also present results for natural gas of the San Joaquin Valley which were obtained in Ref. [6].
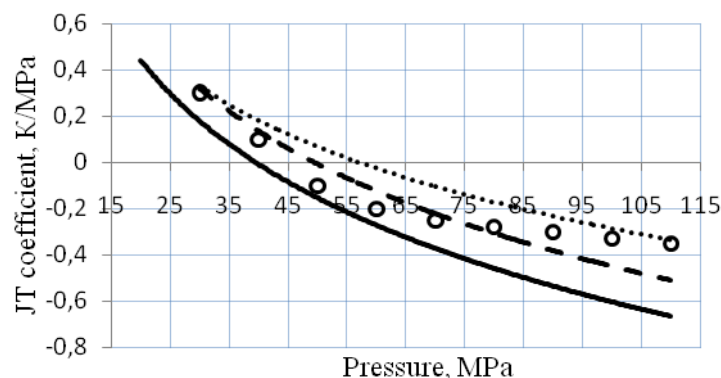
Figure 3. The Joule-Thompson coefficient for methane (●), for ethane (-), for natural gas of the Bavlinskoye deposit (solid line) and for natural gas of the San Joaquin Valley (°) [6] at 463 K.

Table 2. Simulation results and experimental data [7] for the inversion pressure of methane, ethane, natural gas of the Bavlinskoye deposit and of the San Joaquin Valley [6] (T=463K)

| Gas	Simulation, P_{inv}, MPa	Experiment, P_{inv}, MPa
Methane	57	57
Ethane	52	50
Natural gas (Bavlinskoe deposit)	40	-
Natural gas (San Joaquin Valley)	42	42

3.3. Thermodynamic derivative properties
Thermodynamic derivative properties are the second order derivatives of the thermodynamic potential, with respect to other properties such as pressure, molar volume or enthalpy, which are first order derivatives of the thermodynamic potential. In the present work, we have calculated the thermal expansivity (Figure 4), the isothermal compressibility (Figure 5), compressibility factor (Figure 6) and the heat capacity (Figure 7) in a wide range of pressure up to 110 MPa at a temperature of 463 K.

3.4. Phase behaviour
The Figure 8 shows vapour pressure curves for methane and for natural gas of the Bavlinskoye deposit and Figure 9 presents the liquid-vapour phase diagram. For methane we present experimental data (they are marked by crosses). We obtained critical parameters for methane (T_c=190.6 K and P_c=4.6 MPa) and for natural gas (T_c≈310 K and P_c ≈ 8,6MPa). For methane results agree well with experimental data. For multicomponent mixtures of the natural gases the so-called pseudocritical pressure and temperature are the sums of the abundance of each component in the mixture (volume or moles) multiplied by the critical pressure and temperature of the same component respectively. According to this rule for natural gas of the Bavlinskoye deposit we obtained T_c = 284 K, P_c = 4.6 MPa. It should be pointed out that one has very smooth curve for methane and non-smooth curve for natural gas. This discrepancy and the non-smooth behaviour of the phase equilibrium curve for the mixture can be explained by the fact that each component of the mixture changes its phase under different conditions, in other words there is phase separation in the mixture.
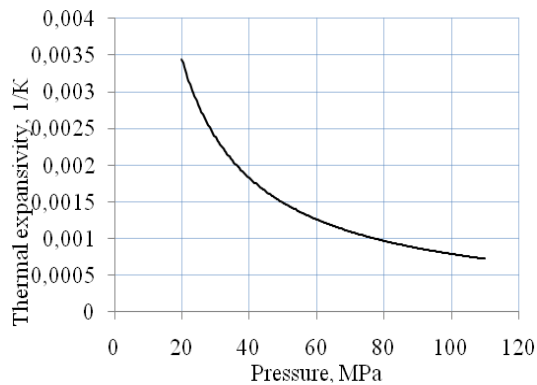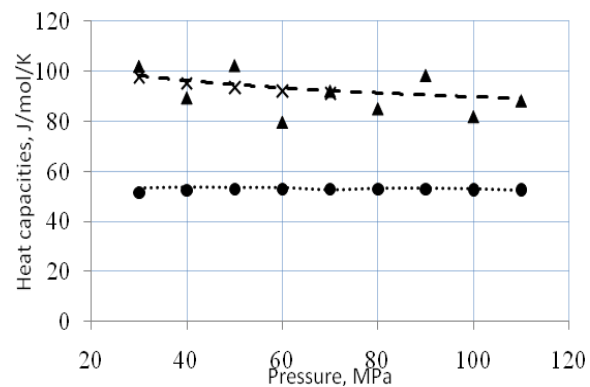
Figure 4. The simulated thermal expansivity of the natural gas of the Bavlinskoye deposit at 463K
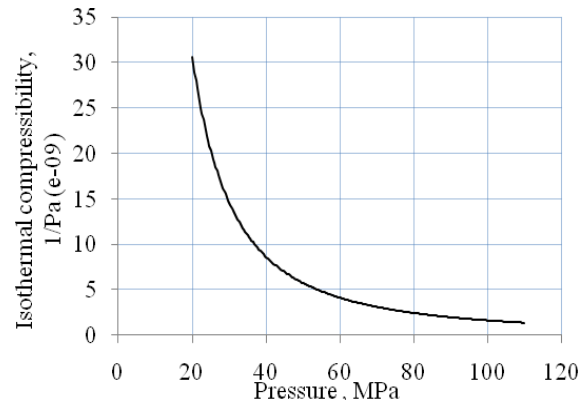
Figure 5. The simulated isothermal compressibility of the natural gas of the Bavlinskoye deposit at 463K.
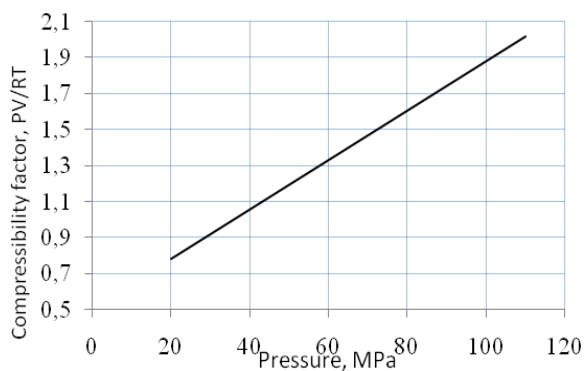

Figure 6. Monte Carlo simulation results for the compressibility factor of the natural gas of the Bavlinskoye deposit at 463K.


Figure 7. Heat capacities of methane, ethane and of the natural gas of the Bavlinskoye deposit (bottom curve is for methane along with experimental data (•) [7], upper curve is for ethane with experimental data (×) [7] and (▲) is for natural gas of the Bavlinskoye deposit).

The ratio of the mole fraction in the gas phase to the mole fraction in the liquid phase for the given component i of mixture is denoted as the K_i. On the Figure 10 the dependence of K_i on the temperature is plotted. It could be seen that nitrogen, carbon dioxide and methane evaporate more intensively from the liquid mixture.
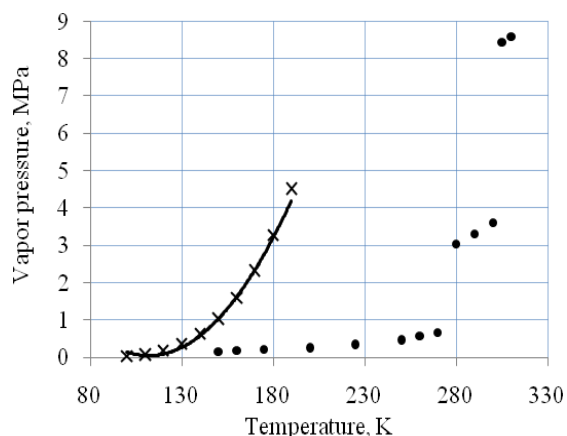
Figure 8. Simulated saturated vapor pressure of natural gas of the Bavlinskoye deposit (•) and of methane (solid line) with experimental data (×) [7].
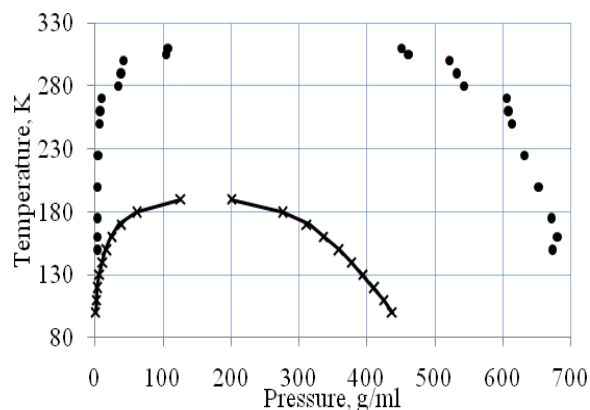
Figure 9. Liquid-Vapour phase diagram of natural gas of the Bavlinskoye deposit (•) and liquid-vapour phase diagram of methane (lower curve) with experimental data (×) [7].
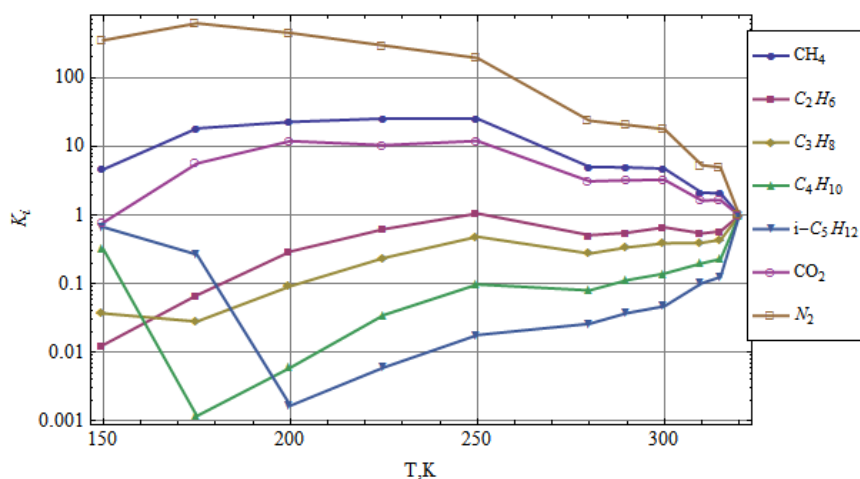
Figure 10. Temperature dependence of the K_i parameter for each component in the mixture (see text for details).

4. Conclusion

To sum up we presented the results of calculations of the basic thermodynamic parameters for the natural gas of the Bavlinskoye deposit and some parameters for methane and ethane: density, Joule-Thompson coefficient and inversion pressure. The known experimental data agree well with our calculations indicating the correct description of these systems by means of molecular simulation.

In a conclusion we should note that methods of molecular simulation in combination with other methods can significantly increase the efficiency of geological and geophysical studies. Computer simulation serves as a theoretical tool that allows to check the findings of existing analytical methods, theories or to supplement their predictions.

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