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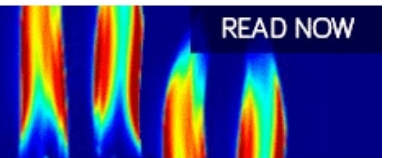
# Compressibility factor of natural gas determination by means of molecular dynamics simulations

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**ABSTRACT**

Forecasting of phase behavior and PVT-properties of natural gas is one of the major tasks during the developing and operation of gas and gas condensate fields. Each stage – from an exploration to transportation and storage of gas is followed by continuous changes of thermobaric conditions. This causes changes of thermodynamic properties of gas, one of which is compressibility factor. The comparative study of the existing theoretical methods of compressibility factor determination is given in the presented work: based on the equation of state and empirical correlations. Besides, the alternative approach based on molecular dynamics simulations with the Lennard-Jones potential is offered. The analysis of the received results is carried out on the basis of 165 experimental data for 5 various mixtures of natural gas covering temperatures of 310.9 – 344.4 K and pressure range of 7.074 - 48.443 MPa. The statistical analysis shows that the molecular dynamics method shows the minimum error and is suitable for determination of z-factor of mixtures with methane content more than 90%. For mixtures with the high content of carbon dioxide the Peng-Robinson equation of state with shift-parameter shows the minimum error.

## I. INTRODUCTION

Development and operation of gas and gas condensate fields is connected with continuous change of thermobaric parameters, in particular, of temperature and pressure. Prediction of phase behavior of natural gas in such conditions becomes one of the main tasks at all stages: production, operating, transportation and sale of natural gas therefore special attention is paid to determination of PVT properties of natural gas. In the majority of engineering calculations for the analysis of PVT properties and phase behavior of natural gas the compressibility factor is used. The most exact way of its definition is experimental.[1] However, natural gas production and transport deals with constant changes in composition and properties. In such conditions experimental studies become time consuming and expensive. Therefore the methods based on use of empirical correlations and the equations of state became one of the main approaches to z-factor determination. There are more than 20 empirical correlations c00the most known of which are Papay,[2] Latonov-Gurevich,[3] Beggs and

Brill,[4] Shell oil company, Bahadori et al.,[5] Heidaryan et al.,[6] Sanjari and Nemati Lay,[7] Shokir et al.,[8] Mahmoud.[9] To find the correlation dependencies experimental data are used that imposes restriction for their applicability. They allow to define correctly properties of gas only in the limited range of pressure and temperatures.[10] Other approach which was widely adopted in the oil and gas industry is calculation of compressibility factor on the basis of the cubic equation of state. This method allows to define natural gas properties in the wide range of pressures and temperatures.[11] The equations of state of Soave-Redlich-Kwong, Peng-Robinson, Patel-Teja, PC SAFT and SAFT-VR Mie are the most widespread.[12,13] They allow to predict the process of oil and gas fields development.[14]

It is possible to carry neural networks,[15,16] genetic algorithms and methods of optimization of the field of particles[17] to new methods of predicting the compressibility factor of natural gas. These approaches are based on a stochastic algorithm of search of the optimum parameters of a system providing the most exact determination of PVT properties.

Macroscopic properties of natural gas are formed under the influence of intermolecular interaction forces. Therefore evolution of such parameters as density, pressure and temperature can be studied at the microscopic level with use of statistical mechanics (Monte Carlo method) and molecular dynamics simulations. In works[18–24] the results of thermophysical properties for pure natural gas components and its mixtures determination by molecular dynamic simulations are presented.

In the current work the molecular dynamics simulations with the Lennard-Jones potential applicability to the prediction of natural gas compressibility factor is considered. The received results are compared to the known experimental data, empirical correlation and equations of state. Also strengths of the proposed approach and the direction of its further development are considered.

## II. METHODS OF COMPRESSIBILITY FACTOR DETERMINATION

In gas industry the compressibility factor is most often determined by formula

$$z = \frac{PV}{nRT},$$

where $P$ is pressure, $V$ is volume, $n$ is the number of gas moles, $R$ is universal gas constant, $T$ is temperature. If to express all parameters of an equation of state through the given variables, then the z-factor can be determined by the law of corresponding states as function of the specified parameters:

$$z = z(P_{Pr}, T_{Pr}),$$

$$P_{Pr} = \sum_{i=1}^{n} y_i P_{C_i},$$

$$T_{Pr} = \sum_{i=1}^{n} y_i T_{C_i},$$

where $y_i$, $P_{C_i}$, $T_{C_i}$ – molar volume and the critical pressure and temperature for molecule $i$.

### A. Empirical correlations

The experimental data for the compressibility factor of hydrocarbon mixtures obtained by various authors became a basis for the correlation dependencies of a z-factor on the given values of pressure and temperatures. Today more than 20 empirical correlations are offered,[6] however, as shown in work,[41] the most exact results show models of Shell Oil Company[25] and Heidaryan.[26] Also in calculations Latonov-Gurevich correlation is widely used.[3]

#### 1. Shell oil company

The correlation dependence of a z-factor on reduced pressure and temperature has an appearance:[25]

$$z = A + BP_{Pr} + (1 - A)\exp(-C) - D\left(\frac{P_{Pr}}{10}\right)^4,$$

$$A = -0.101 - 0.36T_{Pr} + 1.3868\sqrt{T_{Pr} - 0.919},$$

$$B = 0.021 + \frac{0.04275}{T_{Pr} - 0.65},$$

$$C = P_{Pr}(E + FP_{Pr} + GP_{Pr}^4),$$

$$D = 0.122\exp(-11.3(T_{Pr} - 1)),$$

$$E = 0.6222 - 0.224T_{Pr},$$

$$F = \frac{0.0657}{T_{Pr} - 0.85} - 0.037,$$

$$G = 0.32\exp(-19.53(T_{Pr} - 1)).$$

#### 2. Heidaryan et al.

Heidaryan *et al.* developed the correlation dependence allowing to define with high precision compressibility factor of natural gas in the range of reduced pressures $0, 2 \leq P_{Pr} \leq 15$ and temperatures $1.2 \leq T_{Pr} \leq 3$. The dependence has an appearance:[26]

$$z = \ln\left(\frac{A_1 + A_3 \ln P_{Pr} + \frac{A_5}{T_{Pr}} + A_7(\ln P_{Pr})^2 + \frac{A_9}{T_{Pr}^2} + \frac{A_{11}}{T_{Pr}}\ln P_{Pr}}{1 + A_2 \ln P_{Pr} + \frac{A_4}{T_{Pr}} + A_6(\ln P_{Pr})^2 + \frac{A_8}{T_{Pr}^2} + \frac{A_{10}}{T_{Pr}}\ln P_{Pr}}\right).$$

The coefficients $A_1 \ldots A_{11}$ are presented in Table I.

#### 3. Latonov-Gurevich

Russian researchers Latonov and Gurevich in 1969 offered simple correlation for calculation of z-factor:[3]

$$z = (0.4\lg T_{Pr} + 0.73)^{P_{Pr}} + 0.1P_{Pr},$$

which shows good correspondence to experimental data, except for small area where there is a sign change of a derivative of coefficient of imperfection on pressure.[27]

### B. Equations of state

There are different types of equations of states: virial, cubic, complex – the greatest distribution was gained by the cubic equations of state for the simplicity of expression, ability with high degree of accuracy to describe thermodynamic properties of liquids and gases and their phase behavior. Distinguish two, three, four and five parametrical cubic equations of a state. In the oil

**TABLE I**. Coefficients for Heidaryan correlation dependence.

| Coefficient | $0.2 \leq P_{Pr} \leq 3$ | $3 \leq P_{Pr} \leq 15$ |
|---|---|---|
| $A_1$ | $2.827793 \times 10^{+00}$ | $3.252838 \times 10^{+00}$ |
| $A_2$ | $-4.688191 \times 10^{-01}$ | $-1.306424 \times 10^{-01}$ |
| $A_3$ | $-1.262288 \times 10^{+00}$ | $-6.449194 \times 10^{-01}$ |
| $A_4$ | $-1.536524 \times 10^{+00}$ | $-1.518028 \times 10^{+00}$ |
| $A_5$ | $-4.535045 \times 10^{+00}$ | $-5.391019 \times 10^{+00}$ |
| $A_6$ | $6.895104 \times 10^{-02}$ | $-1.379588 \times 10^{-02}$ |
| $A_7$ | $1.903869 \times 10^{-01}$ | $6.600633 \times 10^{-02}$ |
| $A_8$ | $6.200089 \times 10^{-01}$ | $6.120783 \times 10^{-01}$ |
| $A_9$ | $1.838479 \times 10^{+00}$ | $2.317431 \times 10^{+00}$ |
| $A_{10}$ | $4.052367 \times 10^{-01}$ | $1.632223 \times 10^{-01}$ |
| $A_{11}$ | $1.073574 \times 10^{+00}$ | $5.660595 \times 10^{-01}$ |

and gas industry the greatest distribution was gained by Soave-Redlich-Kwong[28] and Peng-Robinson[29] equations of state. Last of them was created as attempt to improve the predicting ability of the Soave-Redlich-Kwong equations of state.

### 1. Peng-Robinson equation of state

The Peng-Robinson equation of state:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b) + b(v - b)},$$

where $a, b$ – coefficients, $v$ – molar volume, $R$ – universal gas constant. Coefficients $a$ and $b$ for pure substances are defined only by properties of substance and are calculated as follows:

$$a = a_c \cdot \phi(T),$$

$$\phi(T) = \left[1 + \psi\left(1 - \sqrt{T/T_C}\right)\right]^2,$$

$$\psi = 0.37464 + 1.54226\omega - 0.26992\omega^2,$$

$$a_c = 0.457235R^2T_C^2/P_C,$$

$$b = 0.077796RT_C/P_C,$$

where $P_C$, $T_C$, $\omega$ – the critical pressure, critical temperature and the acentric factor of pure substance respectively.

### 2. Peng-Robinson equation of state with shift-parameter

During the existence of the Peng-Robinson equation of state more than 220 of its modifications and specifications were offered.[30] They allow to increase the accuracy of determination of such parameters as the absolute pressure, saturation pressure, density of liquid and gaseous phases, heat capacity, etc. Modification[31,32] in which for molar volume $v$ the amendment c is entered: $\widetilde{v} = v - c$, which allows to considerably increase the accuracy of calculation of z-factor. For calculation of $c$ it is recommended to use so-called "shift-parameter" $s$: $c = sb$, provided in Table II.

### C. Molecular dynamics method

One of the modern numerical methods of studying the phase behavior of hydrocarbon systems is the molecular dynamics simulations.[33–35] This approach allows to model directly dynamics of a system and to define its thermodynamic properties. Interaction between molecules is defined by a chosen interaction potential. To simulate the hydrocarbon systems, Mie[36] and Lennard-Jones potentials were widely adopted.[37] The potential function, most known

**TABLE II**. Shift-parameter for natural gas components.

| Component | $s$ |
|---|---|
| $CH_4$ | −0.1595 |
| $C_2H_6$ | −0.1134 |
| $C_3H_8$ | −0.0863 |
| $N_2$ | −0.1927 |
| $CO_2$ | −0.0817 |

**TABLE III**. Parameters for Lennard-Jones potential.

| Component | $CH_4$ | $C_2H_6$ | $C_3H_8$ | $N_2$ | $CO_2$ |
|---|---|---|---|---|---|
| $\sigma$, Å | 3.73 | 4.3 | 4.77 | 3.625 | 3.72 |
| $\varepsilon \times 10^{-21}$, J | 2.042 | 3.33 | 4.28 | 1.32 | 3.258 |

**TABLE IV**. Mixture compositions.

| Mixture | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $CH_4$ | 0.8977 | 0.8520 | 0.7458 | 0.7593 | 0.5841 |
| $C_2H_6$ | 0.0464 | 0.0410 | 0.0474 | - | 0.2867 |
| $C_3H_8$ | - | - | - | 0.1316 | - |
| $N_2$ | 0.0053 | 0.0057 | 0.0052 | - | - |
| $CO_2$ | 0.0506 | 0.1013 | 0.2016 | 0.1091 | 0.1292 |

and simple in realization is the Lennard-Jones intermolecular potential:

$$U^{LJ}(r_{ij}) = 4\varepsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^6\right],$$

where $r_{ij}$ is the distance between molecules $i$ and $j$, $\varepsilon$ is the depth of the potential energy well and $\sigma$ is the distance at which the potential is zero.

In work[38] it is shown that at the corresponding parameters of interaction $\sigma$ and $\varepsilon$, Lennard-Jones potential allows to calculate z-factor for natural gas components, such as methane, ethane, propane, nitrogen and carbon dioxide with a sufficient accuracy. Parameters $\sigma$ and $\varepsilon$ for the considered natural gas components are specified in Table III, and parameters for intermolecular interactions are determined by Lorentz-Berthelot rule: $\sigma_{12} = (\sigma_1 + \sigma_2)/2$, $\varepsilon_{12} = \sqrt{\varepsilon_1\varepsilon_2}$. Details of molecular dynamics simulations and
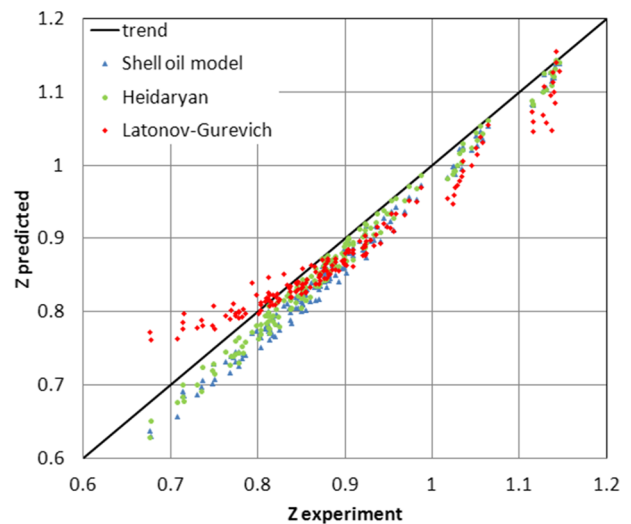


**FIG. 1**. The cross plot for empirical correlation dependencies.

its realization at heterogeneous computing stations are presented in the previous authors' works.[38,39]

The compressibility factor can be determined by molecular dynamics simulations using formula:

$$z = \frac{\frac{Nk_bT}{V} + \frac{1}{3V}\sum_{i=1}^{N-1}\sum_{j>i}\mathbf{r}_{ij}\mathbf{f}_{ij}}{\sum_{k=1}^{n}\frac{m_kN_k}{V}R_kT},$$

where $N, V, T$ – total number of molecules in the system, volume and temperature respectively, $m_k, N_k, R_k$ – mass, number of molecules of $k$ – component and gas constant, $k_b$ – Boltzmann constant, $n$ – number of components, $f_{ij}$ – force acting on a particle $j$ from a particle $i$.

## III. RESULTS

To compare different approaches we use the experimental values of compressibility factor from Buxton.[40] Table IV presents five mixtures in various concentrations of methane, ethane, propane, carbon dioxide and nitrogen. Compressibility factor for them was calculated at temperatures of 310.9 K, 327.6 K and 344.3 K and pressure from 7.07 to 48.44 MPa.

In figure 1 the expected z-factor for each mixture calculated on empirical correlation dependencies of Shell Oil Model, Heideryan and Latonov-Guverich and experimental data for 165 points are represented.

In figure 2 the cross plots of the compressibility factor computed using the Peng-Robinson equation of state and it's modification with shift-parameter are presented. Figure 3 shows the cross plot of the results obtained using the molecular dynamics simulations.

Statistical parameters of the considered models in comparison with experimental data are presented in Table V.

The average absolute relative error for the presented mixtures for different methods is given in figure 4. The cumulative frequency for all mixtures determined by different methods is presented in figure 5. The best result on all mixtures shows a Peng-Robinson equation of state with shift-parameter with an average error in z-factor determination of 1.16% and the coefficient of determination equaled to 0.9881. The maximum error showed the Latonov-Gurevich correlation method, Shell Oil Company and the classical Peng-Robinson equation of state. Molecular dynamics simulations allow to receive the best result and the minimum error of 0.61% for mixtures with the content of methane of 90% and above. It should be
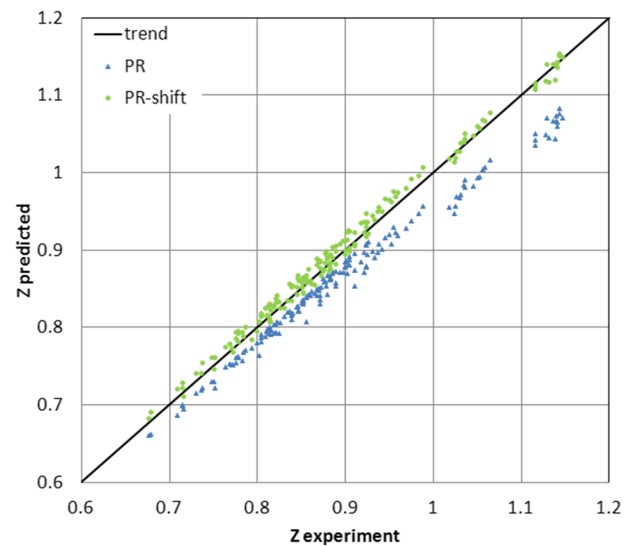


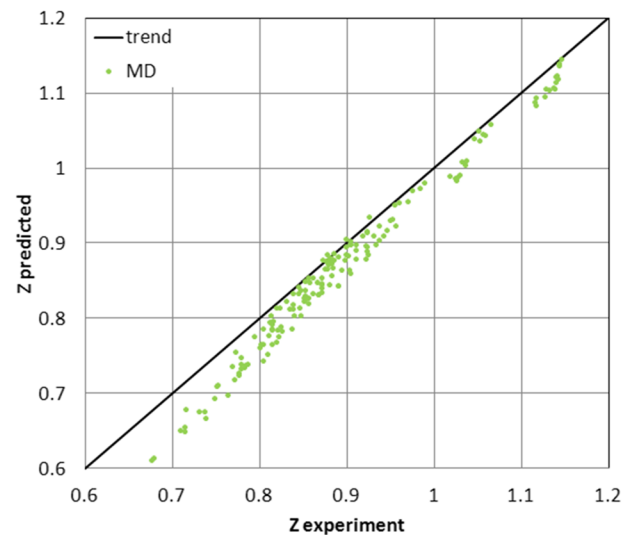**FIG. 2**. The cross plot for the Peng-Robinson equations of state.



**FIG. 3**. Thecross plot for a method of molecular dynamics.

**TABLE V**. Statistical errors of different methods.

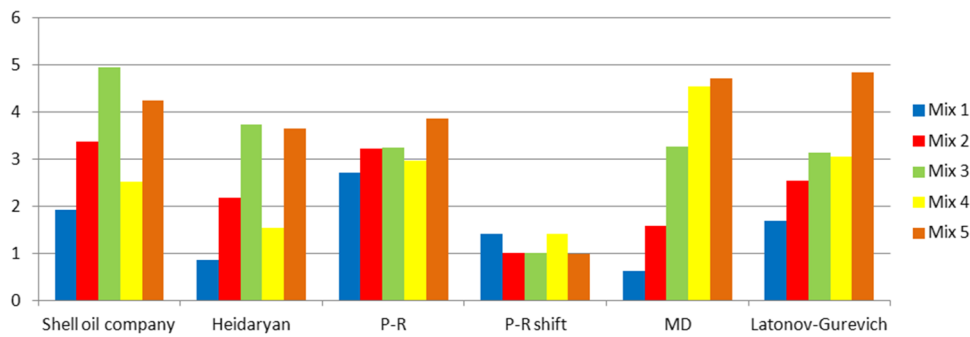| Method | AARE, % | MSE | RMSE | SD | $R^2$ |
|---|---|---|---|---|---|
| Shell oil company | 3.3909 | 0.0010 | 0.0317 | 0.1209 | 0.9307 |
| Heidaryan *et al* | 2.3844 | 0.0006 | 0.0237 | 0.1167 | 0.9584 |
| Latonov-Gurevich | 3.0454 | 0.0011 | 0.0333 | 0.0904 | 0.8637 |
| Peng-Robinson | 3.1949 | 0.0013 | 0.0356 | 0.0991 | 0.8700 |
| Peng-Robinson+shift | 1.1600 | 0.0001 | 0.0118 | 0.1091 | 0.9881 |
| Molecular dynamics simulations | 2.9345 | 0.0009 | 0.0301 | 0.1207 | 0.9376 |

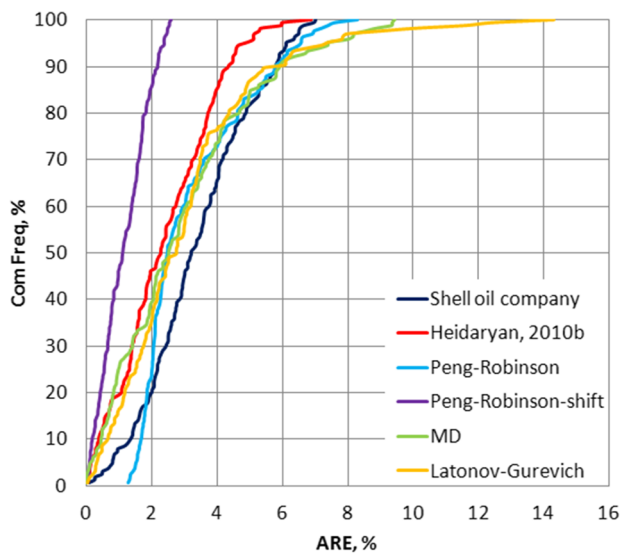FIG. 4. AARE for various mixtures by different methods.



FIG. 5. Cumulative frequency of fractional errors for different methods.

noted that the specified content of methane is characteristic of the majority of gas fields. Figure 3 shows that the value of compressibility factor calculated by molecular dynamics method is underestimated in comparison with experimental data. Obtaining more exact values of a z-factor requires modification of parameters of intermolecular potential and their "setup" on more simple binary and ternary mixtures.

## IV. CONCLUSION

In the presented work different approaches to determination of compressibility factor of natural gas are considered: empirical correlations, equations of state, molecular dynamics simulations. The analysis of results allows to make the following conclusions:

1. The molecular dynamics simulations show the minimum error of 0.61%, for mixtures with the content of methane of 90% and above.
2. The Peng-Robinson equation of state with the shift-parameter shows the minimum error in determination of z-factor for all mixtures considered (1.16%).

3. The greatest error shows the Latonov-Gurevich correlation method, Shell Oil Company and the classical Peng-Robinson equation of state.
4. The molecular dynamics simulations with the classical Lennard-Jones potential is applicable for determination of compressibility factor of mixtures of natural gas, but the increase in accuracy of calculations requires specification of potential parameters.

## ACKNOWLEDGMENTS

## APPENDIX A: STATISTICAL FORMULAS

Average absolute relative error (AARE), %

$$\text{AARE} = \frac{100}{N} \sum_{i=1}^{N} \left( \left| \frac{z_i^{pred} - z_i^{exp}}{z_i^{exp}} \right| \right)$$

Mean square error (MSE)

$$\text{MSE} = \frac{\sum_{i=1}^{N} (z_i^{pred} - z_i^{exp})^2}{N}$$

Root mean square error (RMSE)

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^{N} (z_i^{pred} - z_i^{exp})^2}{N}}$$

Standard deviation (SD)

$$\text{SD} = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} (z_i^{pred} - \text{average}(z_i^{exp}))^2}$$

Coefficient of determination ($R^2$)

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (z_i^{pred} - z_i^{exp})^2}{\sum_{i=1}^{N} (z_i^{pred} - \text{average}(z_i^{exp}))^2}$$

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