

Construction of a Phase Diagram for Binary Helium-Methane Mixture Using Peng-Robinson Equation of State and the Molecular Dynamics Simulations

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Abstract. A detailed algorithm for calculating the vapor-liquid phase equilibrium for multicomponent systems based on the Peng-Robinson equation of state is presented. The procedure for finding the optimal interaction parameters is described on the example of a binary helium-methane mixture. A procedure for constructing a phase diagram using the molecular dynamics simulations with the Lennard-Jones potential is presented. Comparison of the results of calculating the phase equilibrium of the helium-methane mixture obtained using the equation of state, molecular dynamics modeling and experimental data is carried out.

INTRODUCTION

The unique properties of helium made it of great need in various industries: mechanical engineering, metallurgical engineering, rocket engineering, nuclear engineering and space engineering. Today Russian Federation produce helium by separating it from natural gas on the only helium refinery in Orenburg. Discovery of the largest helium deposits, such as Kovyktinskoye, Chayandinskoye, Sobinskoye, Astrakhanskoye, Srednebotuobinskoye, Orenburgskoye, Tas-Yuryakhskoye, makes it possible to develop the helium industry in Russia. However, helium recovery requires tools for modeling natural gas phase behavior.

Analysis, optimization and development of energy-efficient technology for the processing of hydrocarbon raw materials deals with software packages such as Aspen Hysys, Pro / II with Provision, GIBBS, etc. In works [1, 2] it is noted that the specialized software shows sufficient discrepancies with experimental data while simulating the mixtures containing helium. It can lead to incorrect indicators for energy and cold consumption when calculating the technological process of helium concentrate formation. The use of specialized software systems without a clear understanding of the theoretical foundations often does not allow us to understand the details of the ongoing thermodynamic processes.

In [3] it is noted that, despite the large amount of data on phase equilibria, the development of an independent software module for calculating vapor-liquid equilibrium is difficult due to the lack of a clear algorithm. Therefore, the author proposed a sequential algorithm for determining the mole fractions of a multicomponent mixture based on the Soave-Redlich-Kwong equation of state (EOS).

Kasperovich A.G. et al. [4] presented the optimization of the algorithm for constructing the phase diagram of the mixture using a classical spreadsheet editor based on the Peng-Robinson EOS. The paper [5] considers the issue of using parallel algorithms to speed up the modeling of phase equilibria.

Despite the fact that the equations of state are constantly being modified [6], a number of works are aimed to improve the interaction parameters for mixtures [7].

As an alternative to the classical EOS [8] the molecular dynamics simulations and the Monte Carlo method [9] are being intensively developed for constructing the phase diagrams. The modern computing systems has made it possible to use atomistic modeling as a universal tool for studying hydrocarbon systems [10].

In this work, the authors give a detailed description of the algorithm for constructing the phase diagram of a binary mixture based on the Peng-Robinson EOS. The main theoretical points necessary for constructing the phase diagram are noted. A method for determining the optimal interaction parameters is presented for a binary

helium-methane mixture. The key features of using the molecular dynamics simulations with a Lennard-Jones potential for constructing a phase diagram are considered.

THEORETICAL BASIS OF PHASE DIAGRAM CONSTRUCTING

Peng-Robinson equation of state. Today there are dozens of "classical" equations of state, and hundreds of their modifications and improvements [6]. One of the equations that is widely used in modeling the phase state of hydrocarbons is the Peng-Robinson EOS:

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)} \quad (1)$$

where a, b – coefficients, V – molar volume, R – gas constant.

The coefficients a and b for a specific mixture are calculated using the components a_i and b_i for pure gases:

$$\begin{aligned} a &= \sum_{i=1}^N \sum_{j=1}^N n_i n_j (1 - c_{ij}) \sqrt{a_i a_j}; \\ b &= \sum_{k=1}^N n_k b_k; \\ a_i &= a_{ci} \cdot \varphi_i(T); \\ \varphi_i(T) &= \left[1 + \psi_i \left(1 - \sqrt{T/T_{ci}} \right) \right]^2; \\ \psi_i &= 0,37464 + 1,54226\omega_i - 0,26992\omega_i^2; \\ a_{ci} &= 0,457235R^2 T_{ci}^2 / P_{ci}; \\ b_i &= 0,077796R T_{ci} / P_{ci}. \end{aligned} \quad (2)$$

Here i is component index, N – number of components in a mixture, n_i - mole fraction of a component in a gaseous (then $n_i = y_i$) or liquid (then $n_i = x_i$) state, c_{ij} – interaction coefficients, P_{ci} , T_{ci} , ω_i – critical pressure, critical temperature and the acentric factor of the i -th component of the mixture, respectively. The values of the above parameters can be found in the works [8, 11].

Phase equilibrium calculation using the EOS is based on the classical thermodynamics of multicomponent systems. Therefore, to construct a phase diagram, knowledge of such parameters as the compressibility factor and fugacity is required.

Compressibility factor (z-factor). In statistical mechanics the description of the compressibility factor is

$$Z = \frac{PV}{RT}$$

In physics, it is a measure of how much the thermodynamic properties of a real gas deviate from those expected of an ideal gas. The above relation allows to rewrite the equation of state (1) with respect to the z -factor in the form of a cubic equation:

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0, \quad (3)$$

where A, B are defined from:

$$A = \frac{aP}{R^2 T^2}; B = \frac{bP}{RT}.$$

The solution of (3) admits the existence of three roots, among which the largest positive root Z_V corresponds to the vapor phase, and the smallest positive Z_L to the liquid phase. In practice, numerical algorithms are used to solve this cubic equation, e.g. Newton's method.

Fugacity. The onset of equilibrium in a thermodynamic system is characterized by fugacity. In general, for any EOS, the logarithm of the fugacity coefficient can be determined by the formula:

$$\ln f_i = \int_V^{\infty} \left[\frac{1}{RT} \left(\frac{\partial P}{\partial n_i} \right) - \frac{1}{V} \right] dV + \ln \frac{n_i RT}{V}.$$

By calculating the integral based on the Peng-Robinson EOS, one can obtain fugacity formulas for the vapor and liquid phases.

For vapor phase:

$$\begin{aligned} \ln f_i^V = & \ln (y_i P) - \ln (z_V - B_m^V) + \frac{B_i^V}{B_m^V} (z_V - 1) \\ & - \frac{A_m^V}{2\sqrt{2}B_m^V} \left[\left(\frac{2 \sum_{j=1}^N a_{ij} y_j}{a_m^V} - \frac{B_i^V}{B_m^V} \right) \ln \left(\frac{z_V + B_m^V (1 + \sqrt{2})}{z_V + B_m^V (1 - \sqrt{2})} \right) \right]. \end{aligned} \quad (4)$$

For liquid phase:

$$\begin{aligned} \ln f_i^L = & \ln (x_i P) - \ln (z_L - B_m^L) + \frac{B_i^L}{B_m^L} (z_L - 1) \\ & - \frac{A_m^L}{2\sqrt{2}B_m^L} \left[\left(\frac{2 \sum_{j=1}^N a_{ij} x_j}{a_m^L} - \frac{B_i^L}{B_m^L} \right) \ln \left(\frac{z_L + B_m^L (1 + \sqrt{2})}{z_L + B_m^L (1 - \sqrt{2})} \right) \right]. \end{aligned} \quad (5)$$

The superscript V and L means the vapor and liquid phases, respectively, and the parameters a_m , b_m , A_m , B_m are calculated by the formulae

$$a_m = \sum_{i=1}^N \sum_{j=1}^N n_i n_j (1 - c_{ij}) \sqrt{a_i a_j}; \quad b_m = \sum_{k=1}^N n_k b_k; \quad A_m = \frac{a_m P}{R^2 T^2}; \quad B_m = \frac{b_m P}{RT}.$$

Phase equilibrium. Phase equilibrium in a thermodynamic system is a state in which the phases of the system under consideration are in thermal, mechanical and chemical equilibrium, which implies the equality of temperatures, pressures, and chemical potentials for different phases. The classical calculation of the phase equilibrium of the "vapor-liquid" system implies the determination of the component compositions of the vapor and liquid phases for mixtures of a given composition at a given pressure and temperature.

Let us consider an N -component mixture of a given composition z_i , which in an equilibrium state is divided into a vapor phase of composition y_i and a liquid phase of composition x_i . The mole fractions of the vapor and liquid phases are equal to V and L , respectively (hereinafter in the entire work we will use V as the mole fraction of the vapor phase, and not as the volume). The material balance equation for any component will take the form:

$$z_i = V y_i + L x_i$$

Using the ratio $V + L = 1$, and introducing the equilibrium constant $K_i = y_i/x_i$, one can determine the mole fractions of the components by the formulae

$$\begin{aligned} x_i &= \frac{z_i}{V(K_i - 1) + 1}, \\ y_i &= \frac{z_i K_i}{V(K_i - 1) + 1}. \end{aligned} \quad (6)$$

These equations make it possible to determine the mole fractions of the components in the vapor and liquid phases for a mixture of a given composition z_i at known values of K_i and V .

As $\sum_{i=1}^N x_i = 1$, $\sum_{i=1}^N y_i = 1$, then $\sum_{i=1}^N (y_i - x_i) = 0$, and therefore, as K_i is known, one can determine parameter V as follows

$$\sum_{i=1}^N \frac{z_i (K_i - 1)}{V(K_i - 1) + 1} = 0 \quad (7)$$

Depending on the value of V five different cases are possible, each of which characterizes a certain phase state (Table 1).

TABLE 1. Phase states classification

Criterion	Phase type
$V < 0$	Single phase unsaturated liquid state
$V = 0$	Single phase saturated liquid state (boiling point)
$0 < V < 1$	Two-phase vapor-liquid state
$V = 1$	Single phase saturated gas state (dew point)
$V > 1$	Single-phase unsaturated gas state

Equation (7) can have several real roots. However, according to the material balance, only the roots from the interval $[0; 1]$ will have meaning. This equation has N breakpoints. However, between singular points function (7) behaves monotonically, which allows to solve this equation by any numerical algorithm, e.g. the half-division method.

Phase equilibrium computation using the EOS is based on the equality of chemical potentials (fugacities) of the mixture components in all coexisting phases, i.e. the occurrence of the condition $f_i^V = f_i^L$. Knowing the solution to equation (7) allows us to determine the components x_i and y_i , which need to be recalculated iteratively until the equality of fugacities is achieved.

Algorithm

Let us describe the main steps of the algorithm for determining the equilibrium compositions of the vapor y_i and liquid x_i phases, as well as the mole fraction of the vapor phase V based on the Peng-Robinson EOS.

Step 0 (initial data, preparatory)

The initial data are the pressure P , temperature T and the total composition of the mixture z_i . The reference data determine the critical pressures P_{Ci} , temperatures T_{Ci} and the acentric factor ω_i for each component i of the mixture, and also one can calculate the coefficients for Peng-Robinson EOS using the corresponding dependencies (2).

The initial approximation of the distribution coefficients K_i in accordance with the Wilson correlation are calculated from:

$$K_i = \left[\frac{P_{Ci}}{P} \exp(5.373(1 + \omega_i)(1 - \frac{T_{Ci}}{T})) \right]^s.$$

According to the initial data, one of the values 0.25; 0.5; 1; 1.5 is chosen as s . It should be noted, that when studying a binary helium-methane mixture under certain thermobaric conditions, the Wilson correlation requires a slight correction so that the solution existed within the interval $[0; 1]$.

Step 1 (mole fraction of the vapor phase computation)

Equation (7) is solved numerically and the root $V \in [0; 1]$ is found.

Step 2 (components mole fractions computation)

According to (6) x_i, y_i are computed.

Step 3 (compressibility factor of the vapor phase computation)

Equation (3) is solved and the compressibility factor for the vapor phase z_V is found as the largest positive root.

Step 4 (fugacities of the vapor phase computation)

Fugacities of the components in a vapor phase f_i^V are computed using (4).

Step 5 (compressibility factor of the liquid phase computation)

Equation (3) is solved and the compressibility factor for the liquid phase z_L is found as the smallest positive root.

Step 6 (fugacities of the liquid phase computation)

Fugacities of the components in a liquid phase f_i^L are computed using (5).

Step 7 (K_i correction)

Distribution coefficients are corrected by the formula

$$K_i^{(m+1)} = K_i^{(m)} \frac{f_i^L}{f_i^V}, \quad \text{where (m) is number of iteration.}$$

Step 8 (convergence check)

Inequality is checked

$$\left| \frac{f_i^L}{f_i^V} - 1 \right| > \varepsilon, \quad \text{where } \varepsilon \text{ is a specified accuracy.}$$

If this condition is met for at least one component, then return to step 1 and repeat the entire calculation. Otherwise, the problem is solved and the values y_i , x_i , V are determined.

Phase diagram. The phase diagram displays graphically the states of the thermodynamic system in the space of the main parameters - temperature, pressure and composition. For binary mixtures, it is convenient to represent phase diagram in "pressure-composition" coordinates. Diagrams of this type allow illustrating graphically the pressure dependence on the compositions of equilibrated vapor and liquid phases of binary systems at constant temperature.

For this, one should draw boiling and condensation lines, along which $V = 0$ and $V = 1$, respectively. To determine the initial boiling pressure for a given mixture composition at a certain temperature it is necessary to choose an initial point (initial pressure) inside the two-phase region, determine the mole fraction of the vapor phase V in accordance with the algorithm for calculating the phase equilibrium, and the found values of mole fractions x_i and y_i will determine the point on the boiling and condensing lines, respectively.

Determination of the interaction parameters for a helium-methane mixture

The formula for determining the cross interaction coefficients a_{ij} is mainly determined according to the geometric mean rule, however, for greater accuracy, additional refinement coefficients c_{ij} are introduced, which are called interaction parameters

$$a_{ij} = (1 - c_{ij})\sqrt{a_i a_j}.$$

The determination of c_{ij} is based on the best approximation of the vapor-liquid equilibrium, determined by the EOS, to experimental data or, from a mathematical point of view, the search for the minimum of the functional

$$\Phi = \sum_{i=1}^N \left[(x_k^{\text{calc}} - x_k^{\text{exp}})_i^2 + (y_k^{\text{calc}} - y_k^{\text{exp}})_i^2 \right]. \quad (8)$$

For most hydrocarbons, as well as nitrogen, carbon dioxide and hydrogen sulfide, Brusilovsky obtained the values of c_{ij} for all possible pairs [11]. For binary pairs of non-hydrocarbon and hydrocarbon molecules, parameter c_{ij} very often is taken to be zero [3, 12]. It should be noted that many deposits contain up to 1% of helium. However, its content is often ignored and not taken into account in the phase diagrams of natural gases. Critical parameters of helium and acentric factor according to reference data [13] are: $T_c = 5.19$ K, $P_c = 0.227$ MPa, $\omega = -0.365$. Experimental studies of the vapor-liquid equilibrium of the methane-helium system are presented in [14–17]. For the critical parameters mentioned above, the phase diagram of a methane-helium binary mixture at $T = 170$ K and $c_{ij} = 0$ are shown in Fig. 1. Line corresponds to results calculated using the Peng-Robinson EOS, crosses correspond to experimental data from [15]. It is seen that computational results differ significantly from experimental data.

There are only a few works in which the interaction parameter for a helium–methane mixture is given [12, 18]. Therefore, in the presented work, using the Peng-Robinson EOS, we search for the optimal interaction parameter to predict accurately the methane-helium system behavior.

The following procedure is used to find the optimal value of c_{ij} . For a given temperature, the vapor-liquid equilibrium of the binary system is calculated sequentially for values c_{ij} from 0 to 1 with a step of 0.01, and the value of functional (8) is determined. The minimum of the functional $\Phi(c_{ij})$ provides the optimal value of the pair interaction coefficient. It should be noted that c_{ij} significantly depends on temperature, and can often be approximated by a functional dependence.

In [12], it is proposed to abandon the use of the acentric factor ω and the interaction parameter c_{ij} and take them equal to zero, but to re-evaluate the critical parameters of helium T_c , P_c , which are not entirely justified. Therefore, in this work, a calculation was carried out with the optimization of the c_{ij} with the "classical" critical parameters of helium at the acentric factor $\omega = 0$. The results are shown in Fig. 2. It should be noted that at temperatures of 95 K and 125 K there is a significant decrease in the optimal value of the parameter c_{ij} , but this refinement is not significant, since in this case, the value of the potential Φ is corrected only in the 5th digit.

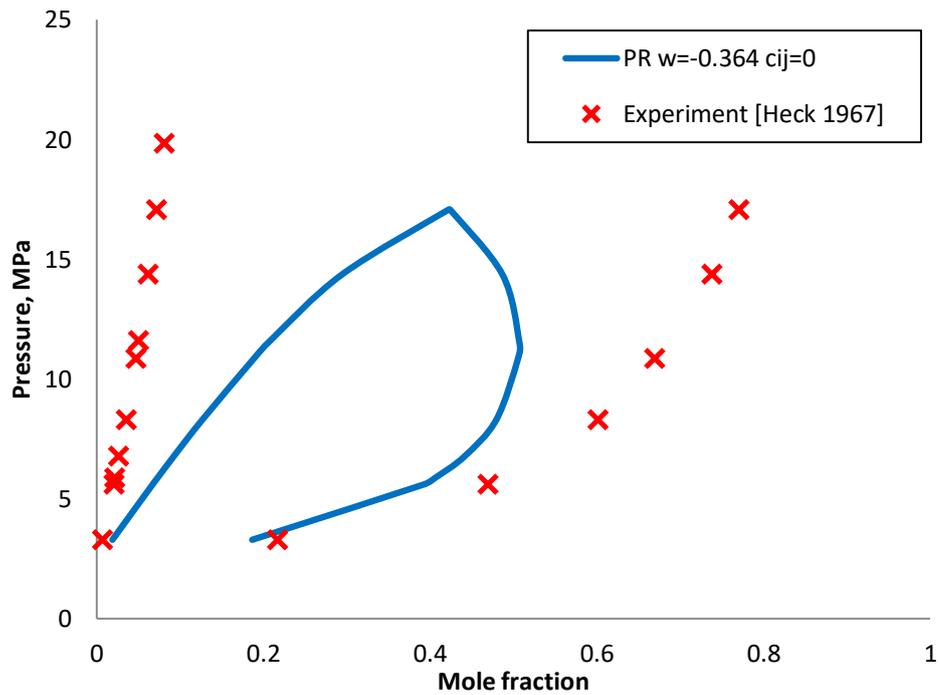


FIGURE 1. Phase diagram at $T = 170$ K

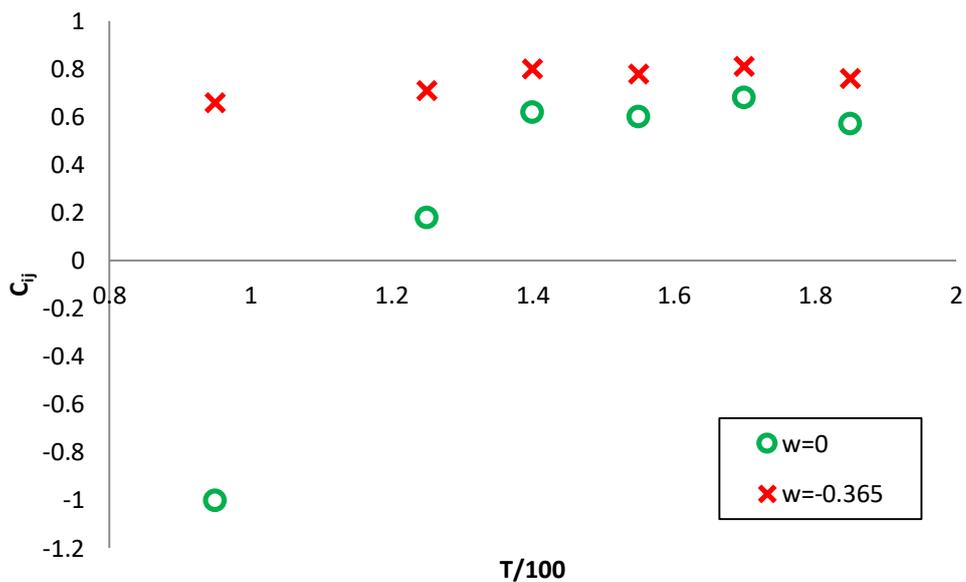


FIGURE 2. Temperature dependence of the optimal pair interaction coefficient c_{ij} at $\omega = 0$ and $\omega = -0.365$

For simplicity, the interaction parameters are assumed as a constant value averaged over all temperatures. The resulting graph of the functional dependence of the discrepancy between the experimental and calculated data according to the Peng-Robinson EOS at temperature range from 95 to 185 K and up to pressures of 20 MPa is shown in Fig. 3.

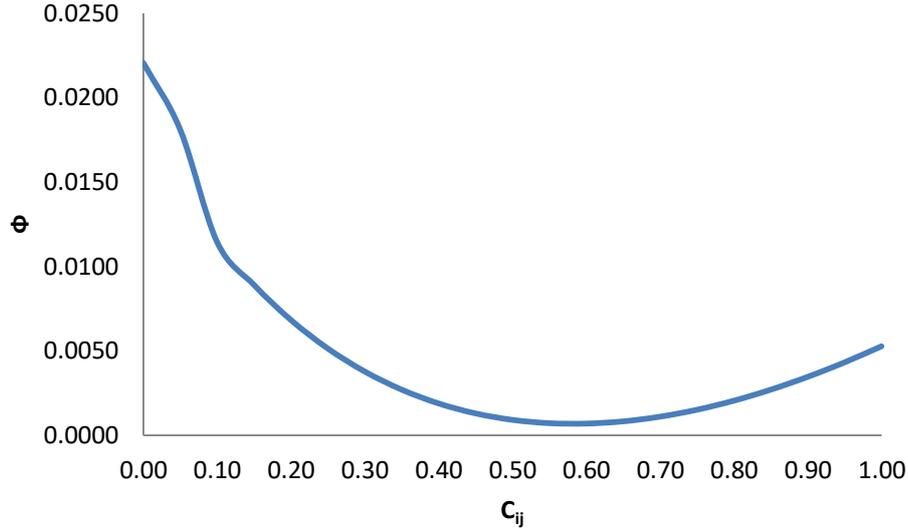


FIGURE 3. The dependence of the functional Φ on the coefficient c_{ij} at $\omega = 0$

The resulting graph allows us to determine the optimal $c_{ij} = 0.58$, which makes it possible to achieve the best fit to the experimental data. Table 2 shows the values of functional Φ for different c_{ij} and ω .

TABLE 2. Values of functional Φ for different c_{ij} and ω .

T, K	Number of experimental points	Φ			
		$\omega = -0.365$		$\omega = 0$	
		$c_{ij} = 0.0$	Optimal c_{ij} (fig. 2)	$c_{ij} = 0.0$	$c_{ij} = 0.58$
95	10	0.0028	7.26×10^{-6}	1.70×10^{-5}	2.47×10^{-5}
125	10	0.0433	3.14×10^{-5}	8.53×10^{-5}	1.94×10^{-4}
140	12	0.0858	4.14×10^{-4}	0.0016	4.50×10^{-4}
155	8	0.2017	3.29×10^{-5}	0.0041	9.32×10^{-5}
170	18	0.4385	7.77×10^{-4}	0.0154	7.50×10^{-4}
185	16	0.4163	3.19×10^{-3}	0.0932	0.002
Average error		0.198067	0.000742	0.019067	0.000585

The table shows that the proposed correction of the pair interaction parameter $c_{ij} = 0.58$ can significantly increase the accuracy of calculations of the vapor-liquid equilibrium for the binary helium-methane system. It is necessary for a qualitative assessment of the country's helium reserves, since extraction of this element is carried out by low-temperature condensation of natural gas and subsequent separation from helium concentrate of such substances as methane, nitrogen, hydrogen, neon, argon.

MOLECULAR DYNAMICS SIMULATIONS

A recent approach that allows one to construct phase diagram is molecular dynamics simulations. It is based on the numerical integration of the equations of motion for each particle of the considered system. The main advantage of the proposed approach is the ability to construct phase diagrams without using experimental data. Among the disadvantages are the computational complexity of the algorithm and stochastic fluctuations of the studied parameters. In addition, the choice of the interaction potential function is not always evident. The potentials TraPPE [19], Mie [20–22], OPLS [23] are widely used to simulate the phase diagrams of hydrocarbon-containing systems. There are also a number of molecular dynamics modeling software packages,

such as GROMACS, LAMMPS, etc., which allow to solve the assigned tasks. Despite its simplicity and a high degree of simplification, the Lennard-Jones potential continues to be used for various kinds of problems [24–27]. In the presented work, an approach to the construction of the phase diagram of a binary helium-methane mixture is proposed based on the molecular dynamics method using the simplest Lennard-Jones interaction potential.

The basis of the molecular dynamics method can be found in [28], and the verification of the authors' algorithm is presented in [29–31]. To construct a phase diagram using the MD simulations, we consider a binary helium-methane system, where the intermolecular interactions are described by the Lennard-Jones potential. The potential parameters for helium and methane are $\sigma_{He} = 2.576 \text{ \AA}$, $\varepsilon_{He} = 0.141 \times 10^{-21} \text{ J}$, $\sigma_{CH_4} = 3.73 \text{ \AA}$, $\varepsilon_{CH_4} = 2.042 \times 10^{-21} \text{ J}$ respectively [32]. Interactions are described by the Lorentz-Berthelot rules. The simulated domain is a parallelepiped with dimensions $80 \times 80 \times 160 \text{ \AA}$. In the central part, the molecules of the system are distributed in accordance with a given concentration. The simulation uses an NVT ensemble, the temperature is maintained by Berendsen thermostat, and the pressure of the system is computed from the virial expansion. The simulation timestep is $4 \times 10^{-15} \text{ s}$. When thermodynamic equilibrium is achieved, the system is stratified into vapor and liquid phases. Numerical density is determined by subdividing the area along the Z axis into 100 layers, in each of which the corresponding number of particles is determined. The distribution of the number density for a binary system consisting of 6400 particles of methane, 1600 helium at a temperature of 170 K is shown in Fig. 4.

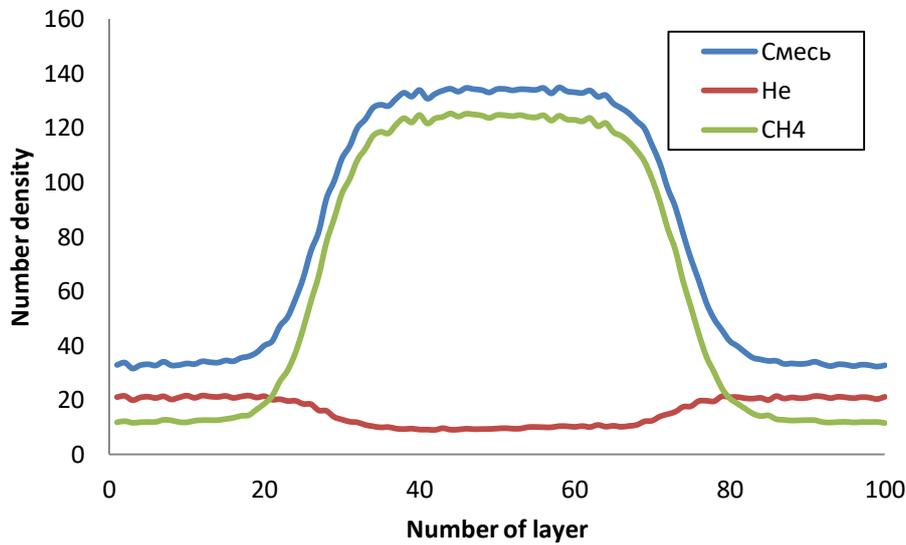


FIGURE 4. Number density distribution along Z

The density distributions were averaged in the interval of steps 100,000 - 200,000. From the data obtained, the mole fraction of a component in the vapor and liquid phases is easily determined based on the numerical density by the formulae

$$x_{He} = \frac{n_{He}^l}{n^l}, y_{He} = \frac{n_{He}^v}{n^v},$$

where n^l , n^v – number density of the system in liquid and vapor phases. It corresponds to central and boundary parts of the simulated domain, n_{He}^l , n_{He}^v – number density of helium in liquid and vapor phases respectively.

For different geometrical dimensions of the modeled system, the results obtained for the equilibrium mole fractions are shown in Fig. 5, together with experimental data and analytical results obtained using the Peng-Robinson EOS.

The results show that the proposed approach using the Lennard-Jones potential describes the gas phase with satisfactory accuracy and has significant discrepancies in describing the liquid phase. Therefore, for a more accurate description of the vapor-liquid equilibrium, either adjustment of the parameters of the Lennard-Jones potential or the use of other potentials, such as potentials of the TraPPE or Mie type, is required.

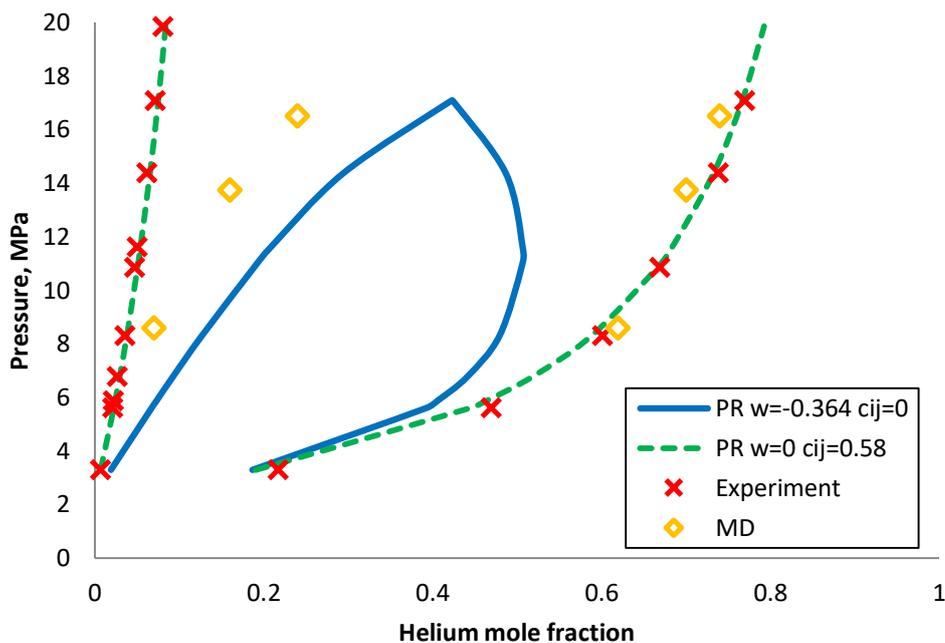


FIGURE 5. Comparison of different methods for constructing a phase diagram

CONSLUSION

The work describes a detailed algorithm for calculating thermodynamic equilibrium and a method for constructing a phase diagram based on the Peng-Robinson equation of state. By the example of a binary helium-methane mixture, the procedure for finding the optimal value of the pair interaction coefficient is described. Calculations of the thermodynamic equilibrium of a binary mixture using the molecular dynamics method are presented. Comparison of the results of calculating the phase equilibrium of the "helium-methane" mixture obtained using the equation of state, molecular dynamics modeling and experimental data is carried out.

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DESIGNATIONS

P – static pressure, MPa;

R – specific gas constant, J/(kg K);

T – static temperature, K;

V – molar volume, m³/mole;

a, b – Peng-Robinson equation of state coefficients;

c_{ij} – interaction parameters;

f – fugacity, MPa;

K – equilibrium constant;

ω – acentric factor;
 Z – compressibility factor;
 z – initial mixture composition;
 x – mole fraction of the liquid phase;
 y – mole fraction of the vapor phase;
 Φ – functional of error;
 σ, ε – Lennard-Jones parameters;

INDICES

i, j – component number;
 m – iteration number;
 c – critical parameter;
 L – liquid phase;
 V – vapor phase;
calc – computed values;
exp – experimental values;

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