Low-parametric equation for calculating the methane viscosity coefficient of liquid, gas and fluid states

A B Kaplun, O S Dutova and A B Meshalkin
Kutateladze Institute of Thermophysics SB RAS, Lavrentiev ave., 1, Novosibirsk, 630090 Russia
E-mail: kaplun@itp.nsc.ru

Abstract. A low-parametric equation for calculating the CH₄ viscosity coefficient in liquid, gaseous, and fluid states was derived using previously obtained unambiguous dependence of the “excess” viscosity of liquids and dense gases on the density of internal energy. The equation describes the viscosity of methane at the temperatures from 91 K to 620 K and pressures of up to 50 MPa in the limits of experimental error.

1. Introduction
Methane is the main component of natural gas in most fields and an important source of raw materials for the chemical industry, where it is used to produce hydrogen, alcohols, synthetic rubber, a number of solvents and many other products. It is widely used as domestic and industrial fuel. Thus, to meet the demands of modern technology, reliable information on the physical, thermodynamic and transport properties of gaseous and liquid methane in wide pressure ranges is needed, both at low and high temperatures.

The most recent correlations of the thermodynamic properties have been reported [1-2]. The equation of state [2] extends over the fluid state up to 620 K and 1000 MPa and is characterized by a high reliability on the basis of excellent experimental data. In addition to the thermodynamic properties [2], the experimental transport property values of methane from the triple point up to 400 K and 55 MPa for the viscosity as well as up to 600 K and 100 MPa for the thermal conductivity were correlated. However, the transport property data are not of the same high accuracy as the thermodynamic data. The available experimental viscosity data of methane at low and high densities have been critically assessed. Experimental data on the viscosity of methane at low and high densities were analyzed in [3]. The new experimental values have been used together with the most reliable data from the literature to deduce a zero-density viscosity correlation for the temperature range from the triple point to 1050 K as well as representation for the higher densities of residual viscosity from the triple point up to 620 K and 100 MPa. The uncertainty ascribed to the viscosity surface is within ±3% in the thermodynamic ranges, for which primary experimental viscosity data are available. A new theory for viscosity modeling based on the friction concepts of classical mechanics was presented in [4]. The friction theory approach links the viscosity of a fluid to its equation of state (EOS), and it is known, gives good results for a large number of compounds over wide ranges of the temperature and pressure. As it is shown in [5], this simple theory can provide accurate modeling within experimental error even using simple cubic EOS. This model has four parameters for correlation of the rarefied gas and 18 parameters for the excess viscosity.
Various versions of equations for calculating the viscosity allow us to describe the experimental data in a wide range of the state parameters. However, they include a large number of coefficients, which increases significantly when trying to describe simultaneously the viscosity of gas and liquid.

2. Equations for calculating viscosity in a wide range of parameters

Using the previously established dependence of excess viscosity \( \Delta \eta = \eta(T, P) - \eta_{en}(T, \rho) \) on the internal energy density \( \Delta U / V \) [6] (see Figure. 1), a simple single low-parameter equation was obtained to describe the viscosity coefficient in a wide range of the state parameters [7]

\[
\eta_{cal}(T, P) = Ax \exp \left( \alpha \frac{x_0}{x_0 - x} \right) + B \left( \frac{T}{T_C} \right)^{0.25} \left( \frac{x}{x_0} \right)^{0.5} \exp(-\beta x / x_0) + \eta_{en}, \tag{1}
\]

where the first term is due to momentum transfer through the intermolecular interaction (the “field” mechanism), the second is the “mixed” mechanism, and the third one contributes to the momentum transfer during the “collisions” of the particles; \( \eta_{en}(T, \rho) = \eta_0(T)\psi(b\rho) \) is the viscosity of hard sphere system by Enskog formula; \( \eta_0(T) \) is the viscosity of dilute-gas; \( \psi(b\rho) \) is density function; \( x = \Delta U / V \) is density of interaction energy; \( \Delta U = U_{ig}(T) - U(P, T) \) is interaction energy; \( U_{ig}(T) \) is internal energy of ideal gas; \( U(P, T) \) is internal energy of system in a given state; \( x^0 = H_0^0 / V_0^0 \), \( V_0 = \lim_{T \to 0, P \to 0} (V(T, P)) \) is hypothetical volume supercooled to absolute zero of liquid, \( H_0^0 = U_{ig}(0) - U(0,0) \) is evaporation enthalpy at absolute zero temperature and zero pressure; \( T_C \) is the critical temperature; \( A, \alpha, B, \beta \) are individual adjustable constants of a substance.

![Figure 1. Dependence of the excess viscosity \( \Delta \eta \) on the internal energy density \( x = \Delta U / V \): 1 – table and experimental data of [8–14], 2 – calculation by equation \( \Delta \eta_{cal} = Ax \exp(\alpha x_0/(x_0 - x)) \).](image)

The procedure of calculating the excess viscosity \( \Delta \eta \) at each point of the thermodynamic surface is as follows. Using the numerical method, we calculate the density or use the reference table data in the density, enthalpy and internal energy for those \( T \) and \( P \), at which it is necessary to find the coefficient of viscosity. Then the viscosity of the system of hard spheres is calculated according to Enskog \( \eta_{en}(T, \rho) \).
\(\rho (T, P)\) at the same temperature and density at which the viscosity of the substance is measured (or taken from the tables) at a given temperature and pressure \(\eta (T, \rho (T, P))\). At each point the excess viscosity is calculated \(\Delta \eta_{\text{tab}} (T, \rho (T, P)) = \eta (T, \rho (T, P)) - \eta_{\text{en}} (T, \rho (T, P))\). Let us distinguish the contribution to the excess viscosity due to the mixed momentum transfer mechanism: the collision (by Enskog) and the field one. To do this, we subtract \(\delta \eta\) found by approximating these initial data by the equation \(\delta \eta = Ax \exp (\alpha x_0 / (x_0 - x))\) from the initial data for excess viscosity \(\Delta \eta_{\text{tab}} (T, \rho (T, P))\). The coefficients are calculated by the least squares method. We assume that the obtained difference \(\Delta \eta = \Delta \eta_{\text{tab}} - \delta \eta\) is due to the mixed - collisional and field - interaction mechanism, which can be written down as \(\delta \eta = B \left(\frac{T}{T_C}\right)^{0.25} \left(\frac{x}{x_0}\right)^{0.5} \exp (-\beta x / x_0)\).

The description of the experimental data, close to optimal, is achieved at \(b = V_0\). The values of \(V_0\) and \(H_{00}\) are usually given in the tables of the thermodynamic properties of substances. In this case, the equations for viscosity (1) contain only four empirical constants \(A, \alpha, B, \beta\). In the case when there are no data on \(V_0\) and \(H_{00}\) the number of the empirical coefficients in equations (1), which must be found from the data on viscosity, increases to 6: \(A, \alpha, B, \beta, V_0\) and \(x_0\).

The equation (1) describes the dependence of the viscosity of a liquid and a gas of a wide range of substances mainly within the experimental error.

3. Calculation of the viscosity coefficient for methane

The results of calculation of the coefficients of liquid, gas and fluid viscosity by equation (1) for methane are presented below. We emphasize that in order to use equations (1) to calculate the viscosity coefficient, it is necessary to have sufficiently accurate thermal and caloric equations of state to calculate the thermal and caloric properties of a substance. All initial information on these properties is taken from [8].

Analysis of the experimental and tabular data showed that the greatest discrepancies are in the region of low temperatures and high pressures. So the discrepancy between the tabular data of different authors at the temperatures of about and below 100 K and pressures of up to 50 MPa reaches ± 8%. Therefore, for our calculations, we used the most accurate experimental [9–14] and table data [8] in the temperature range from 100 to 620 K and pressures of up to 50 MPa.

To calculate the coefficient of the viscosity of a system of hard spheres according to Enskog \(\eta_{\text{en}}\), we used the equation for dilute gas viscosity \(\eta_0 [4]: \eta_0 = d_0 + d_1 T_1 + d_2 T_1^2\). Where \(T_1 = T / T_C\) is the reduced temperature; \(d_0 = 0.00260536, d_1 = -0.0185247, d_2 = 0.0234216\).

In the calculations, the value \(H_{00}\) obtained in [15] was used. The coefficient \(V_0\) found by the Filippov-Timmermans rule \(V_0 / V_C = Z_C, Z_C\) is the compressibility factor. The results of the methane viscosity calculation are given in the Table and in figures 2-4. The Table shows the physical parameters of methane (parameters of the characteristic points) and the values of the coefficients \(A, B, \alpha, \beta, H_{00}, V_0, x_0\), which are necessary for calculating the viscosity using equations (1), ranges of the description parameter, as well as rms \(\sigma, \% = 100 \sqrt{\sum (\eta_{\text{cal}} - \eta_{\text{tab}}) / \eta_{\text{tab}}^2} / (N - 4)\) and weighted average AAD, \(\% = 100 \sum (\eta_{\text{cal}} - \eta_{\text{tab}}) / \eta_{\text{tab}} \right) / (N - 4)\) the deviations of the calculated methane viscosity values from the table values [8].

Figure 2 shows the values of the coefficient of viscosity calculated by formula (1) according to the temperature and pressure on the isobars in comparison with the tabular data from [8]. Figures 3-4 show deviation of methane viscosity calculated from (1) tabular [8] and experimental data [9–14].
Table 1. Physical parameters of methane; coefficients $A$, $\alpha$, $B$, $\beta$, $H_0$ and $V_0$, in equations (1) for calculation of viscosity; ranges of description parameters: by temperature $\Delta T$, pressure $\Delta P$, mean-square $\sigma$ and weighted-mean AAD deviations of calculated viscosity values from initial data [8].

| Parameters | CH$_4$ |
|------------|--------|
| $T_c$, K   | 190.564 |
| $P_c$, MPa | 4.599  |
| $\rho_c$, kg m$^{-3}$ | 162.66 |
| $T_{tr}$, K | 90.685 |
| $\rho_{tr}$, kg m$^{-3}$ | 451.48 |
| $A$, 10$^{-12}$ s | 0.1260044 |
| $\alpha$ | 0.589119 |
| $B$ | 7.10 |
| $\beta$ | 19.66238 |
| $x_0 = H_0/V_0$, MPa | 325.31 |
| $H_0^0$, J g$^{-1}$ | 572.6 |
| $b=V_0$, cm$^3$ g$^{-1}$ | 1.7601746 |
| $\Delta T$, K | 90.685…620 |
| $\Delta P$, MPa | 0.1…50 |
| $\sigma$, % | 2.11 |
| AAD, % | 1.44 |

Figure 2. Comparison of methane viscosities (lines) on isobars, calculated by formula (1) with tabular data of [8] (symbols). 0.05 MPa (1), 0.1 MPa (2), 0.5 MPa (3), 2 MPa (4), 4 MPa (5), 5 MPa (6), 8 MPa (7), 10 MPa (8), 20 MPa (9), 50 MPa (10).
Figure 3. Deviations of viscosity on isobars, calculated by formula (1) from the tabular data of [8] for methane depending on the temperature. 0.05 MPa (1), 0.1 MPa (2), 0.5 MPa (3), 1 MPa (4), 2 MPa (5), 4 MPa (6), 5 MPa (7), 8 MPa (8), 10 MPa (9), 20 MPa (10), 50 MPa (11).

As the analysis has shown, the discrepancies between the viscosity values, calculated by (1) and taken from the Tables (averaged experimental) of [8] do not generally exceed ± 3%, which does not exceed the discrepancies between the experimental viscosity data of other authors. As it can be seen from figures 3-4, a noticeable increase in the discrepancies between the calculated by (1) and tabular viscosity values from [8] and experimental data of [9-14] (up to 4–6%) takes place both in the region of critical temperatures and pressures, and at low temperatures and high pressures. However, in this area the experimental and tabular data obtained by other authors also differ significantly.

Figure 3. The deviations of the experimental data from calculated according to (1) viscosity values for methane in the pressure range of up to 80 MPa and temperatures of up to 620 K. 1 – Diller (1980); 2 – Giddings et al (1966); 3 – Meshcheryakov (1954); 4 – Huang et al (1966); 5 – Chuang et al (1976); 6 – Carmichael et al (1965).
Conclusion
A low-parametric single equation has been obtained for calculating the viscosity coefficient of CH₄ in liquid and gaseous states; this equation describes the viscosity of methane in the temperature range of up to 620 K and pressures of up to 50 MPa. This equation contains four individual empirical coefficients that must be found from the experimental or tabular data on viscosity. It is shown that the values of viscosity calculated by the equation (1) are consistent with the experimental and tabular data within the experimental errors.

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