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PREDICTION OF THE TRANSPORT PROPERTIES OF MULTICOMPONENT DENSE GAS MIXTURES

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Summary: *An implementation of the Thorne–Enskog equation for the evaluation of the thermal conductivity and viscosity of high-density fluid mixture is presented. The method is based upon the rigid-sphere model of the fluid mixture suitably interpreted to apply to real fluids. The procedure requires the knowledge of the transport properties of the pure component gases at high density, the zero-density values of the transport properties both for the pure components and for their binary mixtures, and the knowledge of the virial coefficients. No dense mixture data are required. The computational method is tested against a body of experimental data on thermal conductivity obtained in the Institute of Thermomechanics in measurements on two samples of the natural gas in the temperature interval from 288 K to 360 K for pressures from 0.1 MPa to 15 MPa.*

Key words: *natural gas, thermal conductivity, gas mixtures*

1 Introduction

The gas industry is one of the fields where knowledge of thermophysical properties is needed for a wide variety of applications. Areas of applications are the flow metering and process simulations such as gas-storage simulation, the evaluation of compressor performance tests, the design of interstage cooler and energy-flow measurements. In particular, values of the thermal conductivity are required in the development and calibration of sensors for the measurement of mass and energy fluxes, based on the thin-film anemometry. As the thermal conductivity and viscosity measurements for each particular natural gas composition are not practicable, computational methods for prediction of the transport properties of gas mixtures inevitably should be applied.

The most advanced theoretical results for dense fluid mixtures in regions of state removed from the critical, are those originally proposed for the viscosity by Di Pippo *et al.* [1] and for the thermal conductivity by Mason *et al.* [2]. They are based upon application of the Thorne–Enskog equations for the transport properties of a fluid mixture composed of N species of rigid spherical molecules. The most recent version of that internally consistent procedure for the evaluation of the background transport properties of dense gas mixtures has been developed by Vesovic and Wakeham [3], [4].

In the Institute of Thermomechanics in Prague, a computer code based on the Thorne–Enskog equation has been developed making possible predictions of viscosity and thermal conductivity of multicomponent mixtures of gases from the pure component properties and some

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properties of their binary mixtures. The input properties have been collected from literature for the main components of natural gases: methane, ethane, propane, isobutane, normal butane, carbon dioxide and nitrogen.

2 Theory

The result of Mason *et al.* [2] can be written in the form

$$\lambda_{\mathrm{mix}} = \lambda_{\mathrm{mix}}(\mathrm{tr}) + \lambda_{\mathrm{mix}}(\mathrm{int}), \tag{1}$$

in which $\lambda_{\mathrm{mix}}(\mathrm{tr})$ denotes the contribution of the translational energy transport to the thermal conductivity and $\lambda_{\mathrm{mix}}(\mathrm{int})$ denotes the contribution of the internal energy transport. The translational component of the thermal conductivity for a mixture of N components is given by the formula of the revised Enskog theory for mixtures

$$\lambda_{\mathrm{mix}}(\mathrm{tr}) = -\frac{1}{\det(L)} \begin{vmatrix} L_{11} & \dots & L_{1N} & y_1 \\ \vdots & & & \vdots \\ L_{N1} & \dots & L_{NN} & y_N \\ y_1 & \dots & y_N & 0 \end{vmatrix} + \kappa_{\mathrm{mix}}, \tag{2}$$

where

$$y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{2 m_i m_j}{(m_i + m_j)^2} x_j \gamma_{ij} \chi_{ij} \rho \right], \tag{3}$$

$$\begin{aligned} L_{ii} &= \frac{x_i^2 \chi_i}{\lambda_i^0} + \\ &+ \sum_{j=1, j\neq i}^{N} \frac{x_i x_j \chi_{ij}}{2\lambda_{ij}^0 A_{ij}^* (m_i + m_j)^2} \left(\frac{15}{2} m_i^2 + \frac{25}{4} m_j^2 - 3 m_i^2 B_{ij}^* + 4 m_i m_j A_{ij}^* \right), \end{aligned} \tag{4}$$

$$L_{ij}(i \neq j) = -\frac{m_i m_j x_i x_j \chi_{ij}}{2\lambda_{ij}^0 A_{ij}^* (m_i + m_j)^2} \left(\frac{55}{4} - 3 B_{ij}^* - 4 A_{ij}^* \right), \tag{5}$$

$$\kappa_{\mathrm{mix}} = \frac{32}{9\pi} \rho^2 \sum_{i,j=1}^{N} \frac{m_i m_j x_i x_j \chi_{ij}}{(m_i + m_j)^2} \lambda_{ij}^0(\mathrm{tr}) \gamma_{ij}^2 \chi_{ij}. \tag{6}$$

Here ρ is the molar density of the fluid mixture, x_i and x_j are mole fractions, $\lambda_{ij}^0(\mathrm{tr})$ is the low density thermal conductivity of a hypothetical pure gas of molecular mass $2m_i m_j/(m_i + m_j)$ whose molecules interact according to the real *i*-*j* interaction, and A_{ij}^* and B_{ij}^* are dimensionless ratios of collision integrals [5].

The γ_{ij} are corrections for free-path shortening in an *i*-*j* collision and are calculated from the interaction second virial coefficients B_{ij}. If data are lacking on B_{ij}, the interaction parameters can be estimated from the pure-gas γ_i and γ_j by the rigid-sphere combining rule, which yields

$$\gamma_{ij} = \frac{1}{8} \left(\gamma_i^{1/3} + \gamma_j^{1/3} \right)^3. \tag{7}$$

The pure component quantities γ_i are derived from the second virial coefficients B_i of the real gas:

$$\gamma_i = \frac{6}{5}\left(B_i + T\frac{\mathrm{d}B_i}{\mathrm{d}T}\right). \tag{8}$$

The pseudoradial distribution functions χ_i [2] are calculated from the measured thermal conductivity λ_i of the pure dense gas using the rigid-sphere relation for the thermal conductivity:

$$\chi_i(n,T) = \frac{\beta[\lambda_i - \rho^2\gamma_i^2\lambda_i^0(\mathrm{tr})]}{2n^2\gamma_i^2\lambda_i^0(\mathrm{tr})}\left\{1 - \left[1 - \frac{2\lambda_i^0/\beta}{\lambda_i - \rho^2\gamma_i^2\lambda_i^0(\mathrm{tr})}\right]^{-1/2}\right\}, \tag{9}$$

where

$$\frac{1}{\beta} = \frac{1}{4} + \frac{8}{9\pi}. \tag{10}$$

The rigid-sphere combination rule when applied to the pure component function χ_i leads to the the following explicit expression for the binary mixture χ_{ij}:

$$\begin{aligned} \chi_{ij}(T,\rho) &= 1 + \frac{2}{5}\sum_{k=1}^{N} x_k(\chi_k - 1) + \\ &+ \left[\frac{6}{5}(\chi_i - 1)^{1/3}(\chi_i - 1)^{1/3}\frac{\sum\limits_{k-1}^{N} x_k(\chi_i - 1)^{2/3}}{(\chi_i - 1)^{1/3} + (\chi_i - 1)^{1/3}}\right]. \end{aligned} \tag{11}$$

The transport of internal energy is treated exclusively as a diffusive process in the present formulation, while the collisional internal energy transport is neglected so that the effect of the elevated densities can be handled within the framework of the rigid-sphere model:

$$\lambda_{\mathrm{mix}}(\mathrm{int}) = \sum_{i=1}^{N}\left[\frac{\lambda_i^0 - \lambda_i^0(\mathrm{tr})}{\chi_i}\right]\left[1 + \sum_{j=1, j\neq i}^{N}\frac{x_j\lambda_i^0(\mathrm{tr})\chi_{ij}}{x_i\lambda_{ij}^0(\mathrm{tr})\chi_i}\right]^{-1} \tag{12}$$

Therefore, in the limit of zero density, equations (2)–(12) do not reduce to the most accurate formulation of the thermal conductivity of gas mixture [6] but instead to the so-called Hirschfelder–Eucken diffusional formula. The effect of such an approximation is not large because the contribution of inelastic collisions to the thermal conductivity of gas is typically 1–2 %.

The corresponding formulae for the viscosity are quite analogical to that of the thermal conductivity with λ_i and λ_i^0 replaced by η_i, η_i^0. As the internal degrees of freedom has no effect on the momentum transport, $\lambda_i^0(\mathrm{tr})$ should be replaced by η_i^0.

3 Implementation

In order to compute the thermal conductivity of mixtures on the basis of the above mentioned formulae the following quantities are required: the pure-gas thermal conductivities λ_i at the same molar density as the mixture, the low-density thermal conductivities λ_i^0 and their translational components $\lambda_i^0(\mathrm{tr})$ for the pure gases, the second virial coefficient $B_i(T)$ and its first temperature derivative for each component pure gas, and the mixture low-density parameters $\lambda_{ij}^0(\mathrm{tr})$, A_{ij}^*, B_{ij}^*.

In the comparisons presented here, the interaction quantities $\lambda_{ij}^{0}(\mathrm{tr})$, A_{ij}^{*}, B_{ij}^{*} and $B_i(T)$ have been taken from the correlations of the extended law of corresponding states [7], [8]. The pure gas thermal conductivities for methane, ethane, propane, carbon dioxide and nitrogen have been taken from transport property correlation schemes published, respectively, by Friend et al. [9], [10], Younglave *et al.* [11], Vesovic *et al.* [12] and Stephan *et al.* [13].

4 Results

To test the ability of the procedure to predict the thermal conductivity, the computed values have been first compared with the experimental data on the thermal conductivity of methane-nitrogen mixture obtained by Kestin *et al.* [14] for three mixture compositions. The results of our calculations, in the form of full curves, are compared with the experimental data in Fig. 1. The calculation seems to underestimate the true value at low density which might indicate that the principal source of the discrepancy lies in the representation of the mixture properties at low density. On the other hand the discernible tendency for the difference to change sign at higher densities should be ascribed to the specific features of the present procedure, that incorporate the density dependence.

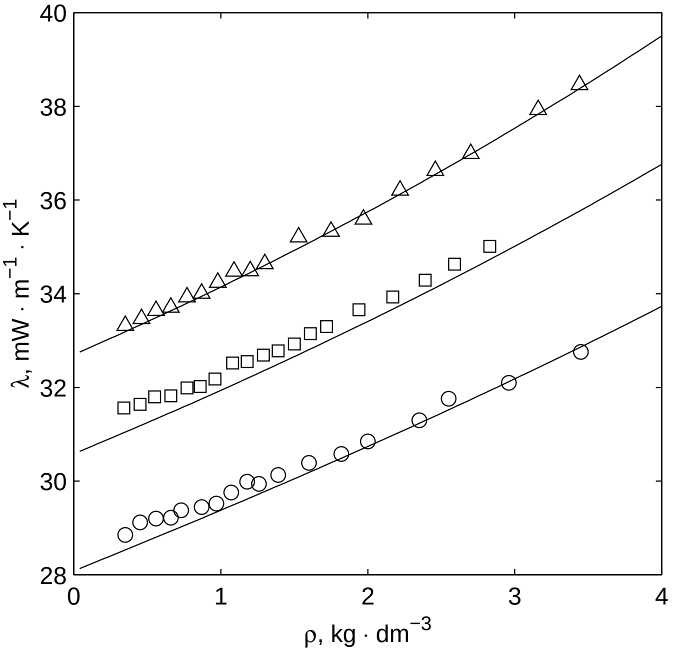

Figure 1: The thermal conductivity of Ne–Ar mixtures at 300.65 K [14]. Comparison between measurement and calculation; x_{CH_4}: ○ 0.2564, □ 0.5432, △ 0.7707.

We have previously reported measurements of the influence of the density upon the thermal conductivity for two samples of natural gases of Norwegian and Russian type [15]. The results of the calculation of the thermal conductivity of the Norwegian natural gas are given in Fig. 2 in the form of straight plots of the thermal conductivity as a function of density, where they are compared with the experimental data. Figure 3 shows the deviations of the predicted thermal conductivity from the experimental values as a function of density. The deviations between

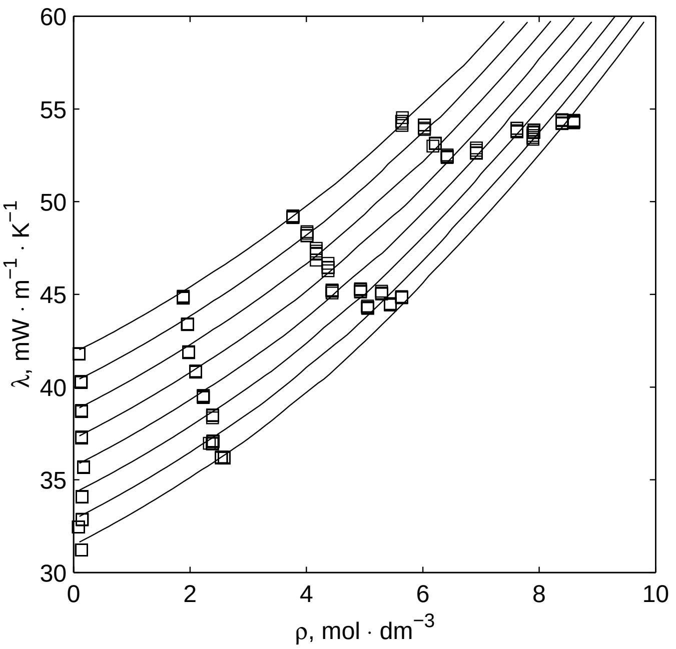

Figure 2: Comparison of calculated (curves) and experimental (□, [15]) thermal conductivities of the Norwegian natural gas for isotherms from 290 K to 360 K.

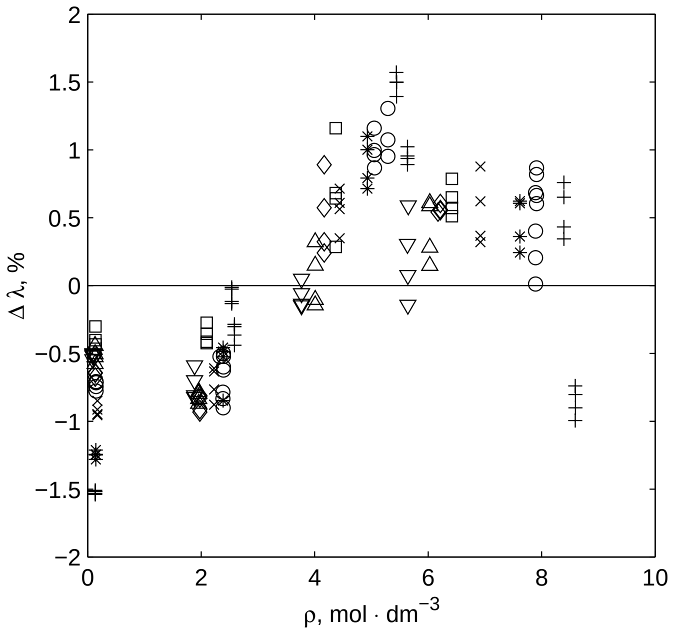

Figure 3: Deviations of the experimental thermal conductivities of the Norwegian natural gas [15] from the values predicted by the present procedure as a function of molar density; + 290 K, ○ 300 K, ∗ 310 K, × 320 K, □ 330 K, ◊ 340 K, △ 350 K, ▽ 360 K.

the experimental data and the prediction do not exceed ±1.6 %. The density dependence of the thermal conductivity is generally represented rather well and the overall discrepancies are within the combined uncertainties of the natural gas thermal conductivity data and those for the pure-component representation employed.

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