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The Prediction of the Viscosity of Dense Gas Mixtures[1]

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An extension of an earlier procedure for the evaluation of the viscosity of very dense gas mixtures is proposed. The scheme is based upon the rigid-sphere theory of dense fluids, which is modified to take into account the behavior of real gases in a self-consistent manner. In particular, it is shown that a pseudoradial distribution function for each pure gas constructed from pure component viscosity data is a smooth function of density and is well behaved in limits of both high and low density. The method proposed removes the restrictions on the range of applicability of earlier methods. Comparisons with the limited amount of experimental information available indicate that the procedure allows evaluation of the viscosity of gas mixtures to within a few percent.

KEY WORDS: high density; mixtures (gas); prediction; viscosity.

1. INTRODUCTION

The *ab initio* prediction of the viscosity of a dense gas mixture, or for that matter, of a dense pure gas, remains an unsolved problem. However, the industrial requirement is, frequently, for the evaluation of the viscosity of a dense gas mixture for which the pure-gas properties are available. In such a case the demands placed upon the theory are less, so that a rather simple theoretical model may be employed.

The best of these models [1] is based on using expansions developed

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for gases consisting of rigid spheres to predict the properties of a mixture by interpolating between the property values for its pure components. Unfortunately, the earlier implementations [1] of this method had several limitations which made the scheme inapplicable under certain important conditions. First, the earlier method used thermodynamic data to obtain an effective size parameter of a molecule. In some cases, this estimate of the size is inconsistent with the transport property data, and as a consequence, the method often fails at high densities. In this paper, following a suggestion of Sandler and Fiszdon [2], choice of the effective size parameter consistent with the transport property data is employed.

Second, the original implementation of the procedure [1] made use of an ad hoc hypothesis to eliminate unphysical behavior of one of the functions characterizing the system. Here, we proposed a procedure which retains the correct physical behavior without the need for the arbitrary choices of the earlier method.

Third, the original procedure [1] employed a rule for the combination of the pure-gas radial distribution functions which has subsequently been found to be thermodynamically inconsistent with the equation of state for a multicomponent gas mixture. A new rule, based on the Percus–Yevick integral equation [3] for the pair distribution function of rigid-sphere molecules, has been derived by Kestin and Wakeham [4]. They employed it for the prediction of the thermal conductivity of gas mixtures at moderate densities and it is applied here in the prediction scheme for the viscosity of dense gas mixtures.

2. THEORY

According to the method of Di Pippo et al. [1] the viscosity of a dense gas mixture containing N components can be written in the form

$$\eta(\rho, T) = -\begin{bmatrix} H_{11} & \cdots & H_{1N} & Y_1 \\ \vdots & & \vdots & \vdots \\ H_{N1} & \cdots & H_{NN} & Y_N \\ Y_1 & \cdots & Y_N & 0 \end{bmatrix} \Bigg/ \begin{bmatrix} H_{11} & \cdots & H_{1N} \\ \vdots & & \vdots \\ H_{N1} & \cdots & H_{NN} \end{bmatrix} + K_{\mathrm{mix}} \quad (1)$$

$$Y_i = x_i \left[1 + \sum_{j=1}^{N} \frac{m_j}{(m_i + m_j)} x_j \alpha_{ij} \bar{\chi}_{ij} \rho \right] \tag{2}$$

$$H_{ii} = \frac{x_i^2 \bar{\chi}_{ii}}{\eta_i^0} + \sum_{\substack{j=1 \\ j \neq i}}^{N} \frac{x_i x_j \bar{\chi}_{ij}}{2\eta_{ij}^0 A_{ij}^*} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} + \frac{4m_j}{m_i} A_{ij}^* \right] \tag{3}$$

$$H_{ij}(j \neq i) = -\frac{x_i x_j \bar{\chi}_{ij}}{2\eta_{ij}^0 A_{ij}^*} \frac{m_i m_j}{(m_i + m_j)^2} \left[\frac{20}{3} - 4A_{ij}^* \right] \tag{4}$$

$$K_{mix} = \left(\frac{16}{5\pi} \right) \frac{15}{16} \rho^2 \sum_{j=1}^{N} \sum_{i=1}^{N} x_i x_j \bar{\chi}_{ij} \alpha_{ij}^2 \eta_{ij}^0 \tag{5}$$

where ρ is the molar density, x_i and x_j are mole fractions of species i and j, and m_i and m_j their molecular masses. A_{ij}^* is a weak functional of intermolecular potential for i–j interactions and is readily available using the corresponding-states principle [5]. The symbol η_i^0 represents the viscosity of pure component i in the dilute-gas limit, while η_{ij}^0 represents the interaction viscosity for species i–j, defined only in the same limit. The parameter α_{ij} accounts for the mean free path shortening for an i–j collision in a dense gas, whereas $\bar{\chi}_{ij}$ is the pseudoradial distribution function for the molecules i and j in the presence of all other species in the mixture.[3]

In order to implement the procedure described above for the evaluation of the mixture viscosity values of $\bar{\chi}_i$ for pure gas, the pseudoradial distribution for the various pure gases are required. These may be obtain from the pure-component viscosity by application of the rigid-sphere expression for the viscosity of a pure gas [1, 4] in the form

$$\bar{\chi}_i(\rho, T) = \frac{\beta}{2} \frac{[\eta_i - \rho \alpha_{ii} \eta_i^0]}{\rho^2 \alpha_{ii}^2 \eta_i^0} \pm \beta \left[\left(\frac{\eta_i - \rho \alpha_{ii} \eta_i^0}{2\rho^2 \alpha_{ii}^2 \eta_i^0} \right)^2 - \frac{1}{\beta \rho^2 \alpha_{ii}^2} \right]^{1/2} \tag{6}$$

$$\frac{1}{\beta} = \frac{1}{4} + \left(\frac{16}{5\pi} \right) \frac{15}{16} \tag{7}$$

where η_i is the pure-component viscosity at the molar density ρ and temperature T at which the properties of the mixture are required.

However, there are three factors that complicate the evaluation of $\bar{\chi}_i(\rho, T)$ using Eq. (6). First, we are required to select values of α_{ii} before solving for $\bar{\chi}_i$, and even when they are selected, Eq. (6) can develop values of $\bar{\chi}_i$ that are complex in certain circumstances. Given that this behavior is physically unrealistic, we must adopt a method which suffers from neither of these disadvantages.

The best method of this kind is that suggested by Sandler and Fiszdon [2]. We note that Eq. (6) has two possible solutions: $\bar{\chi}_i^+$ for the positive sign, and $\bar{\chi}_i^-$ for the negative sign. The first of these solutions, $\bar{\chi}_i^+$, has the property that as $\rho \to 0$, $\bar{\chi}_i^+ \to \infty$, which is physically unrealistic, whereas $\bar{\chi}_i^- \to 1$ as $\rho \to 0$. The second of these solutions, $\bar{\chi}_i^-$, has the property that

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[3] A typographical error in the corresponding equations of Ref. 1 is corrected here.

$d\bar{\chi}_i^-/d\rho < 0$ for large ρ, which is equally unrealistic, whereas $\bar{\chi}_i^+$ has a positive gradient for large ρ. Thus, it is proposed that the most appropriate $\bar{\chi}_i$ is obtained by using $\bar{\chi}_i^-$ at low densities and $\bar{\chi}_i^+$ at high densities, switching between the two at some, as yet unspecified, density ρ^*.

In order to make the switch smoothly it is essential that at the crossover density ρ^*

$$\bar{\chi}_i^+(\rho^*, T) = \bar{\chi}_i^-(\rho^*, T) \tag{8}$$

These equalities lead to the results that

$$\frac{\eta_i}{\eta_i^0 \alpha_{ii} \rho^*} = \left(\frac{2}{\sqrt{\beta}} + 1\right) = 3.1954 \tag{9}$$

Now the group $(\eta_i/\eta_i^0 \alpha_{ii} \rho)$ as a function of density displays its minimum value at the density ρ^*, where the minimum value is

$$\left(\frac{\eta_i}{\eta_i^0 \alpha_{ii} \rho}\right)_{\min} = \left(\frac{\eta_i}{\eta_i^0 \alpha_{ii} \rho^*}\right) = \left(\frac{2}{\sqrt{\beta}} + 1\right) \tag{10}$$

Thus, from experimental, or correlated, values of $\eta_i(\rho, T)$ it is possible, by plotting $(\eta_i/\eta_i^0 \rho)$ as a function of ρ for each temperature, to locate the density of the minimum, $\rho^*(T)$ and to determine the value of the corresponding group at the minimum. Subsequently, application of Eq. (10) yields a value of α_{ii}. In this way we ensure that values of $\bar{\chi}_i$ will be entirely real and that the transition between the two roots is accomplished smoothly.

In practice, the procedure is implemented by establishing the density for which

$$\left(\frac{d\eta_i}{d\rho}\right)_T = \frac{\eta_i}{\rho} \tag{11}$$

Figure 1 shows the pseudoradial distribution function for N_2 deduced according to the procedure described above for which the changeover density is at $\rho = 13300\ \mathrm{mol \cdot m^{-3}}$. The resulting $\bar{\chi}_i$ is smooth and physically reasonable.

In order to proceed further, one needs to construct the pseudoradial distribution function $\bar{\chi}_{ij}$ for species i and j in the mixture. This is achieved by implementing the mixing rule first developed in Ref. 4,

$$\bar{\chi}_{ij}(\rho, T) = 1 + \tfrac{2}{5} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1) + \frac{\left\{\frac{6}{5}(\bar{\chi}_i - 1)^{1/3}(\bar{\chi}_j - 1)^{1/3} \sum_{k=1}^{N} x_k(\bar{\chi}_k - 1)^{2/3}\right\}}{(\bar{\chi}_i - 1)^{1/3} + (\bar{\chi}_j - 1)^{1/3}} \tag{12}$$

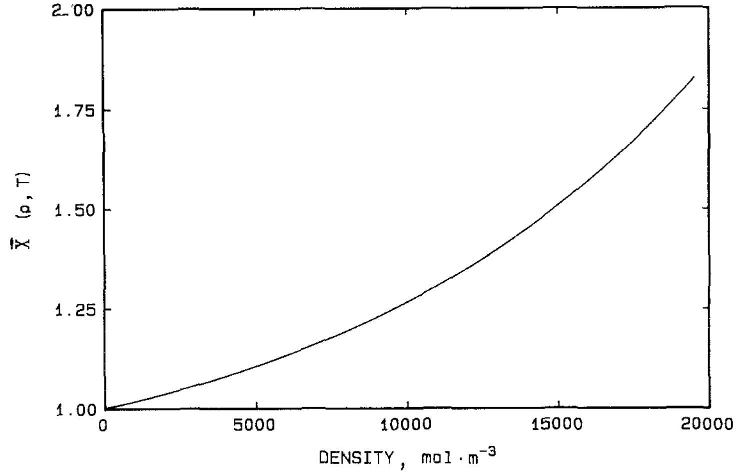

Fig. 1. The pseudoradial distribution function of nitrogen at $T = 200$ K; crossover density $\rho^*_{N_2} = 13300 \text{ mol} \cdot \text{m}^{-3}$.

with the following mixing rule for α's as defined in earlier work [1],

$$\alpha_{ij} = \tfrac{1}{8}(\alpha_{ii}^{1/3} + \alpha_{jj}^{1/3})^3 \tag{13}$$

It would seem at first sight that the scheme proposed for the calculation of viscosity of dense gas mixtures would suffer from the same inadequacies as those of the rigid-sphere model on which it is based. However, that the pseudoradial distribution functions $\bar{\chi}_i(\rho, T)$ at each ρ and T are evaluated [Eq. (6)] using the experimentally available information rather than the results of the rigid-sphere model implies that $\bar{\chi}_i$ is effectively an adjustable function, whose qualitative behavior is that of the rigid-sphere model but whose value has been adjusted according to the pure component property values. It is in this sense that the proposed scheme represents an interpolation of the properties of the pure components.

3. APPLICATIONS

The scarcity of reliable high-pressure measurements of mixture viscosities makes the proposed scheme at the same time useful and difficult to test. Furthermore, the similarity of the present scheme with that proposed earlier [1] makes the repetition of tests at low to moderate densities inappropriate here in the interests of space. Consequently, we prefer to perform comparisons for just two systems which permit a test of the new features of the present scheme associated with the change from one branch of the pseudoradial distribution function to another.

3.1. Viscosity of Air

Direct measurements of the viscosity of air have been correlated by Kadaya et al. [6] and this correlation serves as a suitable data base for comparison. We have therefore calculated the viscosity of air for the properties of its constituents as a function of density over a range of temperature using the scheme described above. For this purpose, air has been treated as a three-component mixture of N_2, O_2, and Ar ($x_{N_2}=0.7841$, $x_{O_2}=0.2066$, $x_{Ar}=0.0093$) and the pure-component viscosities have been obtained using the best available correlations N_2 [7, 8], O_2 [7–9], and Ar [10]. The interaction properties η_{ij}^0, A_{ij}^*, have been obtained using the corresponding-states principle [5].

The results are presented in Fig. 2 for two isotherms and the agreement between calculated and "experimental" data is remarkable since the only empirical information employed is that on low-density binary mixtures and the pure-component viscosities at high density. The

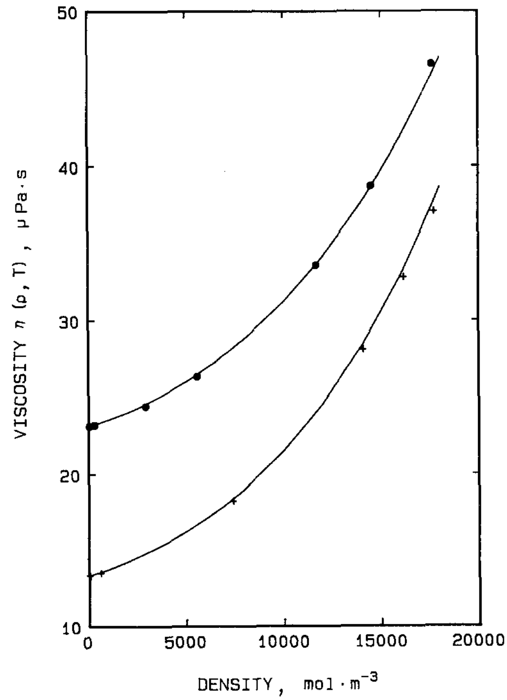

Fig. 2. The viscosity of air. (—) Calculation; (+) experimental at $T=200$ K; (●) experimental at $T=400$ K.

maximum deviations at high density amount to ±1.7%, which is within the experimental uncertainty of the correlation [6]. Furthermore, the crossover density $\rho^*_{N_2}$ ($T = 200$ K) is about 13300 mol · m^{-3}, which is well below some of the densities at which the comparison has been made, so that the proposed scheme is admirably confirmed.

3.2. Carbon Dioxide–Methane System

The viscosity of carbon dioxide–methane mixtures has been measured by De Witt and Thodos [11] in a capillary viscometer and it is believed to be accurate to ±2%. The highest densities correspond to pressures of about 70 MPa. The calculations were performed at 323 K for three different compositions. The properties of pure CO_2 and CH_4 have been obtained using correlations of ref. 12 and 13, respectively. The crossover

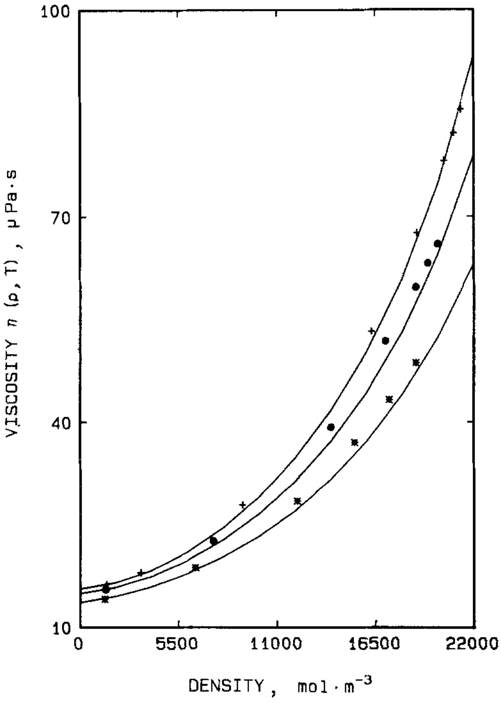

Fig. 3. The viscosity of CO_2–CH_4 mixtures at 323 K. (—) Calculation; (+) experimental for $x_{CO_2} = 0.757$; (●) experimental for $x_{CO_2} = 0.536$; (*) experimental for $x_{CO_2} = 0.245$.

density is about 11000 $\mathrm{mol \cdot m^{-3}}$ for CO_2 and 13500 $\mathrm{mol \cdot m^{-3}}$ for CH_4, again well below the values encompassed by the calculation.

The results are shown in Fig. 3 in the form of a plot of the viscosity as a function of density. Although the agreement is not quite as good as for air, the maximum deviation does not exceed $\pm 5\%$ even though the viscosity changes by almost one order of magnitude within the range considered.

4. CONCLUSIONS

A new self-consistent scheme has been developed for the prediction of the viscosity of dense gas mixtures. It is based on a rigid-sphere theory and on the observation that it is possible to construct a smooth and physically plausible pseudoradial distribution function for real gases by choosing an appropriate solution of the rigid-sphere equations according to well-defined criteria. This modification allows the scheme to be used at very high densities, which has not hitherto been possible.

The scheme has been tested against the limited amount of experimental data available and shown to be capable of reproducing the viscosities of two dense gas mixtures to within a few percent. The application of the same procedure to a wider range of gas mixtures to prove its more general applicability must await more experimental information.

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