

Viscosity Calculation of Supercritical Gases Based on the Rainwater-Friend Theory and the Modified Enskog Theory

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ABSTRACT: A new correlation function for the calculation of viscosity for five typical supercritical gases is presented using the Rainwater-Friend and modified Enskog theory. It is shown that by using accurate values for the thermal pressure and co-volume in the modified Enskog theory, this correlation function is suitable for calculation of the viscosity of supercritical gases, without any density and temperature limitation. For this purpose, two new correlation functions for the calculation of the thermal pressure coefficient and co-volume are presented. It is also shown that the co-volume in the modified Enskog theory depends not only on temperature, but also on density. The accuracy of the calculated viscosity is about 1%, which is much better than the previous work. It is also shown that the modified Enskog theory can be extended to very high density-temperature ranges by choosing correct values for the thermal pressure and co-volume.

KEY WORDS: Co-volume, Modified Enskog theory, Rainwater-Friend theory, Residual viscosity function, Thermal pressure, Viscosity.

INTRODUCTION

The viscosity, η , of fluids is of great interest in various research areas both applied and fundamental. Calculation of the transport properties is clearly simplified when a connection can be made with equilibrium properties. In this context, the Enskog theory [1,2] holds a privileged position for very good reasons [3].

In the derivation of the Boltzmann equation, there are two primary assumptions: (i) only binary collisions are important and (ii) the molecular diameter of the molecules, σ , is small compared to the mean free path of the gas. Both of these assumptions are reasonable for dilute gases but not for dense fluids. Enskog modified the Boltzmann equation in an approximate manner for dense gases [1,2].

Although the Enskog theory is an accurate theory for a hard-sphere fluid, Enskog himself proposed and formulated its application to real dense fluids. This transformation which is known as the modified Enskog theory (MET), presents two modifications with respect to the original Enskog theory. First, the actual pressure p is replaced with the thermal pressure $T(\partial p/\partial T)_p$ in order to take into account the attractive forces among molecules. Second, the co-volume b_0 is redefined in terms of the second and third virial coefficients B and C and their temperature derivatives:

$$b_0 = B + T \frac{dB}{dT} + C + T \frac{dC}{dT} \dots \quad (1)$$

Wakeham and his co-workers [4] found very large dis-

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crepancies between the experimental data for nine simple gases and theoretical predictions of the full MET using the well-known data compilations by Dymond and Smith [5]. The latter step seriously hinders the application of the theory to real systems, because of a lack of knowledge of the virial coefficients for many fluids.

Since the modified Enskog formalism is an "ad hoc theory," these considerations can be interpreted as an additional operation, which completes the procedure. Therefore, the problem is reduced to the specifications of the co-volume and thermal pressure of the systems of interest.

The MET has been applied and tested [6-8] in the supercritical range for only a few substances, although there are some publications for the subcritical domain [9] and mixtures [10-11].

The present paper tries to develop one correlation function for the calculated thermal pressures and another one for the co-volume of supercritical fluids over a wide density and temperature range.

The result of the Enskog theory for viscosity that we use here is [1,2]

$$\eta = \eta_0 b_0 \rho \left[\frac{1}{Y} + 0.800 + 0.761Y \right] \quad (2)$$

In this equation, η represents the viscosity of the hard-sphere fluid, η_0 the viscosity of a dilute hard-sphere gas, b_0 is the co-volume and is equal to $2\pi\sigma^3/3$, where σ is the hard sphere diameter, and $Y = b_0 \rho g(\sigma)$, where ρ is the number density and $g(\sigma)$ is the two-body hard-sphere radial distribution function at contact. The quantity Y is related to the hard-sphere equation of state as [2]

$$Y = \frac{p}{\rho k T} - 1 \quad (3)$$

In spite of the fact that the Enskog theory is strictly a rigid-sphere theory, Enskog showed how the results could be applied to real systems [1,2]. He suggested that instead of relating Y to the actual pressure of the system through Eq. (3), one should introduce the so-called "thermal pressure," $T(\partial p / \partial T)_\rho$, where $(\partial p / \partial T)_\rho$ is called the "thermal pressure coefficient".

The justification for this is that the pressure experienced by a single molecule is made up of two parts, the external pressure, p , due to the walls of the container, and the "internal pressure," $(\partial E / \partial V)_T$, which represents the

force of cohesion of the molecules. The thermodynamic relation relates the sum of these to the thermal pressure. Therefore, we can write Y as

$$Y = \frac{1}{\rho k T} \left[T \left(\frac{\partial p}{\partial T} \right)_\rho \right] - 1 \quad (4)$$

The above equation instead of using Eq. (3) and the dilute gas expression [2] or zero-density values of η_0 give us a complete approximate modification of the Enskog rigid-sphere theory. The main advantage of this method is that the transport properties of the dense gases can be calculated from an equation of state alone.

Now we develop two correlation functions, one for the calculation of the thermal pressure coefficient and the other for co-volume.

CORRELATION FUNCTION FOR THERMAL PRESSURE

One of the most difficult problems within the context of the MET theory lies in the shortage of experimental data for some basic magnitudes such as thermal pressure coefficients which are tabulated for extremely narrow temperature ranges, normally around the ambient temperature for several types of liquids. Furthermore, the measurements of the thermal pressure coefficients made by different researchers often reveal systematic differences between their estimates [12].

These problems have led us to try to establish a correlation function for the accurate calculation of the thermal pressure coefficient for different fluids over a wide temperature and pressure range. The most straightforward way to reach the thermal pressure coefficient is the calculation of $(\partial p / \partial T)_\rho$ using an accurate equation of state which covers wide temperature and pressure ranges. For this purpose, the equations of state for Ar [13], N₂ [14], CO₂ [15], CH₄ [16], and C₃H₈ [16] covering the fluid region over wide temperature and density ranges were used for the calculation of $(\partial p / \partial T)_\rho$.

The calculated thermal pressure coefficients of Ar, N₂, CO₂, CH₄, and C₃H₈ are fitted well into the following empirical correlation function:

$$\left(\frac{\partial p}{\partial T} \right)_\rho = R \rho^* \rho_c \left(1 + \left(a_1 + \frac{b_1}{c + T^*} \right) \rho^* + \left(a_2 + \frac{b_2}{c + T^*} \right) \rho^{*2} \right) \quad (5)$$

where ρ^* and T^* are ρ/ρ_c and T/T_c , where ρ_c and T_c are the critical density and critical temperature of the gas respectively.

The leading term of this correlation function is the thermal pressure coefficient of perfect gas, which each gas obeys at low densities. The coefficients of Eq. (5) are given in Table I. The temperature and density range for each gas and also the average and maximum differences between thermal pressure coefficients by direct derivative of equation of state and correlated values from Eq. (5) are given in Table II.

TABLE I: Coefficients of the Thermal Pressure Coefficient Correlation Function, Eq. (5)

Fluid	a_1	b_1	c	a_2	b_2
Ar	0.5715	-1.012	0.8234	-0.0397	1.367
N ₂	0.1519	2.417	2.013	0.0239	1.057
CO ₂	2.084	-6.670	0.5651	-0.5986	3.865
CH ₄	1.395	-3.626	1.236	-0.4410	2.908
C ₃ H ₈	1.206	-1.281	-0.1189	-0.1142	1.046

TABLE II: Density, Temperature range, Number of Data Points, and Deviations for the Thermal Pressure Coefficients, using Equation of State and Eq. (5)

Fluid	ρ_{\max} (mol. dm ⁻³)	T_{\min} - T_{\max} (K)	$\Delta_{\text{avg. (max)}}$ (MPa / K)	ϵ/k (K)	σ (nm)	No. of points
Ar	45	200-1000	7×10^{-4} (0.07)	143.23	0.3350	115
N ₂	41	150-1000	-2×10^{-3} (0.2)	85.229	0.3728	178
CO ₂	30	400-1100	7×10^{-3} (0.1)	233.03	0.3800	90
CH ₄	29	200-600	1×10^{-3} (0.02)	141.56	0.3791	90
C ₃ H ₈	11	400-600	1×10^{-3} (0.01)	353.35	0.4721	56

CORRELATION FUNCTION FOR CO-VOLUME

As pointed out before, the co-volume b_0 is formally given in terms of the second and third virial coefficients and their derivatives with respect to temperature, Eq. (1). The lack of consistency of these coefficients for many systems is one of the main limitations of applying the MET to real systems. Here we give a correlation function for the calculation of the co-volume b_0 .

In previous work [17,18] it was shown that the most comprehensive theory for the calculation of viscosity in the moderate density range (up to 2 mol.dm⁻³) is the

Rainwater-Friend theory [19,20] which is valid for both monatomic and polyatomic gases. For higher densities, use is made of the empirical observations that the transport coefficient (here viscosity) can always be written [21] as the sum of these contributions

$$\eta = \eta_0 \left(1 + N_A \sigma^3 B_{\eta}^* \rho \right) + D_{\eta} \quad (6)$$

where η_0 is the viscosity at the zero density limit, ρ is the molar density, N_A is Avogadro's constant, σ is the collision diameter and D_{η} is the residual viscosity function which includes the higher density contributions. B_{η}^* is the first order density correction, namely the reduced second virial viscosity coefficient [22],

$$B_{\eta}^* = \sum_{i=0}^6 b_i (T^*)^{-i}$$

where T^* is $\frac{T}{\epsilon/k}$ and

$$b_0 = -0.2201, \quad b_1 = 2.075, \quad b_2 = 5.512, \quad b_3 = -13.91, \\ b_4 = 10.82, \quad b_5 = -4.263, \quad b_6 = 0.5245,$$

the recommended values [18] for σ and ϵ/k are given in Table II. In the previous work, D_{η} was first considered to be density dependent [17] and then density and temperature dependent [18], without stating any theoretical basis for the mathematical form of D_{η} . Here we try to give a somewhat theoretical basis for D_{η} .

It is believed that the MET is a suitable theory for transport properties of non-dilute gases [1,2]. Therefore it is possible to replace D_{η} by the viscosity from the MET theory,

$$D_{\eta} = \eta_0 b_0 \rho \left[\frac{1}{Y} + 0.800 + 0.761Y \right] \quad (7)$$

and then, using Eqs. (6) and (7) yields b_0 as

$$b_0 = \frac{\eta - \eta_0 \left(1 + N_A \sigma^3 B_{\eta}^* \rho \right)}{\eta_0 \rho \left[\frac{1}{Y} + 0.800 + 0.761Y \right]} \quad (8)$$

As Eq. (8) shows, it is possible to calculate b_0 at each density and temperature by knowing η_0 , η and the thermal pressure coefficient via Eq. (5). The accurate viscosity data for Ar [23], N₂ [24], CO₂ [25], CH₄ [16,26] and C₃H₈ [27] over wide temperature and pressure ranges were used via Eq. (8) for the calculation of b_0 at each T and ρ . The calculated b_0 via Eq. (8) with respect to density at different temperatures is shown for Ar in Fig. 1.

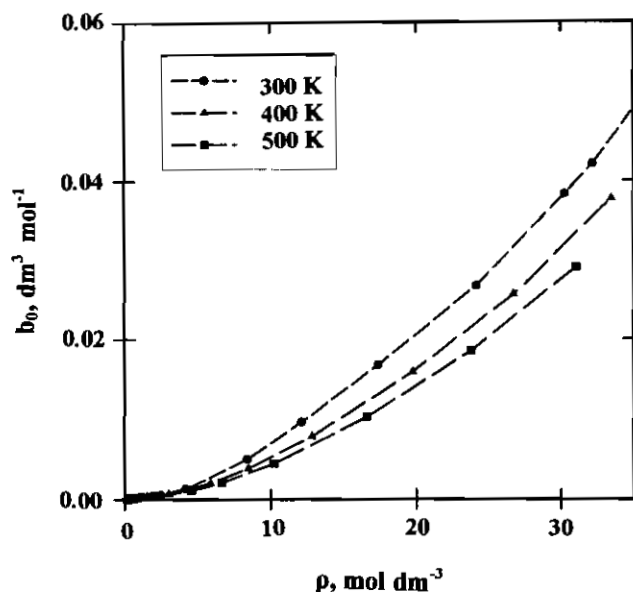


Fig.1: Co-volume of argon according to Eq. (8) with respect to density at different temperatures.

As shown, the density dependency of b_0 is more significant than its temperature dependence. The co-volume b_0 was fitted well with the following empirical correlation function

$$b_0 \rho_c = \sum_{i=1}^5 \left(e_i + \frac{f_i}{T^*} \right) \rho^{*i} \quad (9)$$

where ρ^* and T^* are $\frac{\rho}{\rho_c}$ and $\frac{T}{T_c}$ respectively. The coefficients

Table III: Coefficients of the Co-volume Correlation Function, Eq. (9)

Fluid	e_1	f_1	e_2	f_2	e_3	f_3	e_4	f_4	e_5	f_5
Ar	-0.0144	0.0181	0.1915	0.0506	-0.2902	0.4160	0.1748	-0.3268	-0.0335	0.0689
N ₂	0.0402	-0.0681	-0.0254	0.9050	6.779e-3	-0.8804	0.0682	0.2250	-0.0325	0.0188
CO ₂	-0.7162	1.7790	3.1767	-8.2726	-3.5391	10.2684	1.4790	-4.7106	-2.0401	0.7278
CH ₄	0.0251	-0.0588	0.2391	-0.0442	-0.4551	0.7484	0.2755	-0.5322	-0.0575	0.1112
C ₃ H ₈	9.251e-3	-0.0933	-0.1629	0.9244	0.0740	-0.4105	-7.959e-3	0.0185	1.212e-3	0.0109

Table IV: Average and Maximum Percent Error of the Viscosity Using Eq. (6)

Fluid	Ref.	ρ_{\max} (mol. dm ⁻³)	T_{\min} - T_{\max} (K)	$100 \eta_{\exp}-\eta_{\text{call}} /\eta_{\exp}$ avg. (max)	No. of points
Ar	23	43	300-500	0.80 (4.5)	99
N ₂	24	20	300-1100	0.26 (1.3)	85
CO ₂	25	25	400-1100	1.1 (5.6)	79
CH ₄	16,26	25	200-600	0.84 (4.2)	130
C ₃ H ₈	28	11	400-600	0.40 (2.4)	35

of Eq. (9) and temperature and density ranges for the above gases are given in Tables III and IV respectively.

COMPARISON WITH EXPERIMENTAL DATA

The accuracy of this method in the calculation of the viscosity of supercritical gases is tested in two ways:

a) The calculated values of viscosity based on the modified Enskog and the Rainwater-Friend theory via Eqs. (6), (7), (9) and (4) are compared with the same viscosity data which were used via Eq. (8) for calculation of the co-volume in Table IV. This Table includes the maximum density ρ_{\max} , the temperature range, average (maximum) absolute percent deviation, along with the number of data points. The percent average deviation between the accurate viscosity data at different isotherms of CO₂ [25] and CH₄ [16,26] are also plotted in Fig.(2) over a wide density range. Figure (3) shows the percent deviation between the experimental data and calculated values Δ , % via Eq. (6) for different gases over a wide density range.

b) As an independent test, the calculated values are also compared with some other data for CO₂ [28] and CH₄ [29] which were not used in getting the coefficients of Eq. (8). As Fig. 2 shows the percent average and (maximum) deviations between calculated and experimental values for CO₂ and CH₄ are within the experimental uncertainties.

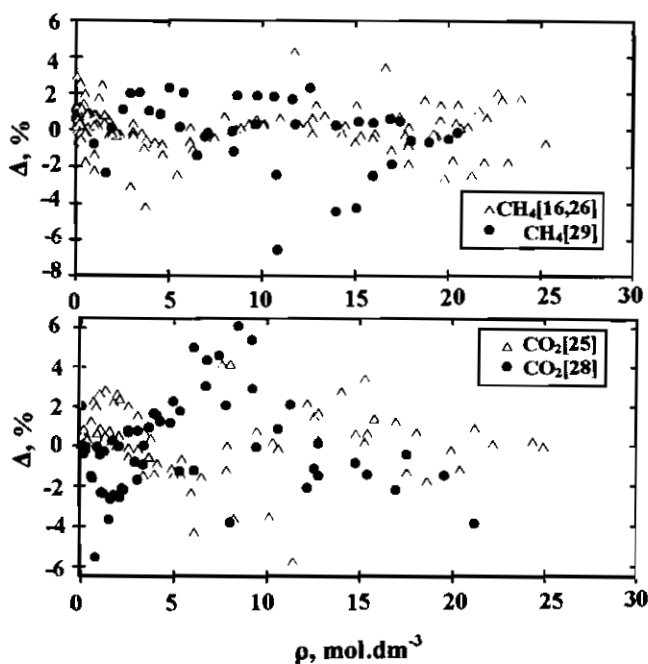


Fig. 2: The percent deviation between the experimental viscosity data for CO_2 [25,28] and CH_4 [16,26,29] and calculated values via Eq. (6) at different isotherms.

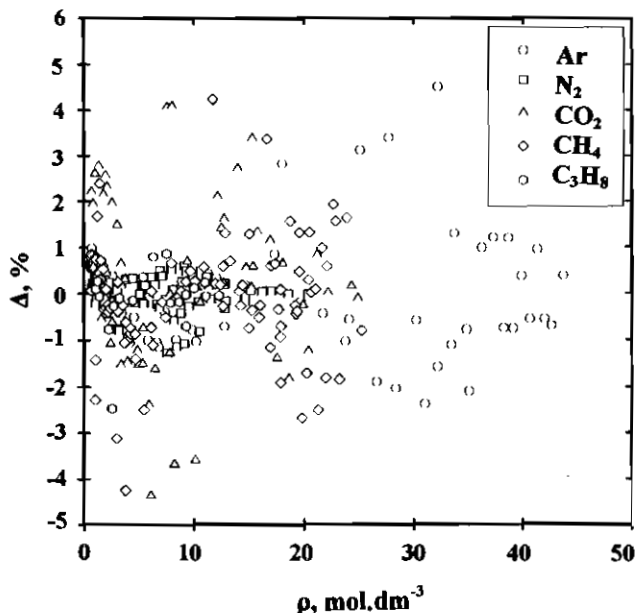


Fig. 3: The percent deviation between the experimental data and calculated values, Δ , % via Eq. (6) for different gases over a wide temperature-density range. The references for experimental data are given in Table IV.

DISCUSSIONS

In this work, the viscosity of 5 typical supercritical gases is obtained using the Modified Enskog theory and the Rainwater-Friend theory. In this scheme two new correlation functions, one for the calculation of the thermal pressure coefficient and the other for the co-volume are obtained. The first is based on the equation of state of the gas and the second on the Rainwater-Friend and the modified Enskog theory.

This correlation function works very well for supercritical gases without any density or temperature limitations with an average deviation between experimental and calculated values of less than 1%. The accuracy of this function is better than the correlation functions used in previous work [17,18]. As Table IV shows, the temperature range validity for CO_2 is about 4 times its critical temperature and the density validity range for Ar is about 3 times its critical density. Therefore, it seems that this function can be applied at any density and temperature by choosing correct values for thermal pressure coefficient and co-volume.

Usually, the co-volume b_0 of the MET is obtained via the virial coefficients and their derivatives, Eq. (1), which depends only on temperature. As pointed out before, this is not a simple procedure mostly due to the absence of accurate of such virial coefficients. But as Fig. 1 shows b_0 are not only temperature dependent, but also density-temperature dependent. Proposing b_0 in this way, Eq. 9, gives accurate values for b_0 , since they are based on accurate values of the viscosity and thermal pressure coefficient.

Precise information about thermal pressure coefficients are scarce, and evaluating it by direct derivative of their equation of state is cumbersome for practical works. The correlation function for this coefficient, Eq. (5) which is based on the accurate equation of states, can calculate easily and accurately this coefficient.

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